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THE THEORY AND PRACTICE
OF
ELECTROLYTIC METHODS
OF
ANALYSIS

BY
DR BERNHARD NEUMANN

ASSISTANT LECTURER ON METALLURGY AT THE TECHNICAL
SCHOOL AT AACHEN

TRANSLATED BY
JOHN B. C. KERSHAW, F.I.C.

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TRANSLATOR'S PREFACE

IN the preparation of the English translation of Dr. Neumann's work on Electrolytic Methods of Analysis a comparatively small number of alterations or corrections have been found necessary ; and the Author's consent has been in every case obtained for the few that have been made.

The portion of the original work dealing with primary and secondary batteries, the dynamo, and the thermo-pile has been omitted. The electro-chemical equivalents have been recalculated upon the most reliable figures for the atomic weights of the elements. The Translator has added a few notes to the original text where such notes were considered to be of utility. These notes are in every case included in square brackets, in order to distinguish them from the original text. The translation is provided with a fairly complete subject index, and a name index, which it is believed will increase the value of the book to those engaged in original research in this branch of chemistry.

With regard to the question of current supply, it may be pointed out that city and town laboratories can obtain the current required from the supply mains of the electric-lighting companies.

The installation of small transformers for reducing the current voltage to five volts, and where necessary for converting alternating currents into direct ones, is a comparatively simple matter. When continuous work is contemplated, the addition of one or two storage batteries would be requisite.

Three warnings may be given to those who through the instrumentality of this book are led to make practical use of electrolytic methods in their laboratories for the first time :—

1. Electrolytic methods should only be used when decided advantages in time or accuracy will result. The practical examples given in Part III., D, clearly indicate the principles upon which electrolysis can be used with advantage in analytical work. The Author's concluding paragraph on page 245 wisely states that it will 'always be found most convenient to combine the chemical and electrolytic methods of separation.' The attempt to carry out complete analyses by means of electrolysis, or to use electrolytic methods for the determination of metals more conveniently estimated by gravimetric or volumetric methods of analysis, will generally result in failure, and may lead the chemist who has not had any experience of the advantages to be gained from these new methods, when rightly applied, to confine himself more rigidly than before to the older methods of analytical work.

2. The greatest care and attention must be given to the precautions, mentioned on page 85, relative to the electrodes. Many failures of electrolytic methods in the hands of students and novices could, no doubt, be traced to neglect of these very elementary conditions of successful work.

3. The conditions as to current density, temperature, and E.M.F. mentioned in the detailed descriptions of the various methods in Part III. must be strictly observed. Slight variations in these conditions will in many cases suffice to entirely alter the nature or character of the deposit.

In conclusion, the Translator hopes that the reception accorded in England and America to the English edition of Dr. Neumann's work may be as favourable as that given to the original in Germany one year ago.

LONDON : *January* 1898.

AUTHOR'S PREFACE

UP to the present time, two works have been published which treat of electrolytic methods of chemical analysis. One of these was written by E. Smith, and has been translated into German by Ebeling; the other was written by A. Classen.

Both of these works deal principally with the authors' own methods, although a few others receive mention.

In the meantime electrolytic methods of analysis have been adopted in many technical laboratories, and have been accepted as valuable aids, and in some cases as useful alternative processes, to the ordinary analytical procedure.

The methods now customarily, and even exclusively, used in these technical laboratories for the determination of different metals, receive in the above-named works only subsidiary mention; the current is given in terms of detonating gas; the voltage is not even mentioned. In the present work these faults and omissions are rectified.

In the consideration of the methods of electrolytic determination of single metals, the methods of greatest technical importance receive the most ample treatment. These are described in detail; exact data regarding current, voltage, and temperature are given, so that even the novice will be in a position to carry them out with some degree of success. The more important of the remaining methods are also noticed briefly, and their relative advantages and disadvantages are discussed.

Following the next division of the work, which is devoted to metal-separations, there comes a subdivision containing a selection of practical examples. In this it is shown that in the analysis of metals, alloys, and smelting works' products, electrolytic methods of analysis have already found acceptance, or could advantageously be adopted.

Since the newer theories relating to electrical phenomena are steadily meeting with more general acceptance, it is certainly fitting that works on electrolysis, both analytical and technical, should be provided with a brief review of them.

The Author has therefore devoted the opening chapters of the present work to such a summary. The phenomena and laws of electrolysis are discussed and explained in the light of the newer theories.

The most convenient forms of current-measuring and regulating apparatus are specially described.

It has been throughout the Author's chief aim to provide both the student and the practical chemist with a work which should cover the whole of the ground ; one which, while it treated fully of the theoretical side of the subject, and gave all the necessary explanation of electrochemical phenomena, should still deal in an unusually full manner with the practical aspects of these new analytical methods, and should enable both the student and practical chemist, by its large number of practical examples, and by its full descriptions of the apparatus and instruments used, to avoid those errors into which they might otherwise fall.

The numerous references to the original literature of the subject may be regarded as a useful appendix to the work.

DR. B. NEUMANN.

STOLBERG : *September* 1896.

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ELECTROLYTIC METHODS

OF

ANALYSIS



INTRODUCTION

IN the year 1792 Volta commenced to investigate Galvani's discovery, and there resulted from his investigations 'the voltaic pile.' Since that time a very large number of arrangements of conductors of the first and second class have been constructed, by means of which it has been possible to produce an electric current with ease. It was therefore natural that the mode of action of the different elements, or piles, should have received close study, and that careful attention should have been given to the attendant phenomena. One of the earliest observations was, that water which had been made acid with sulphuric acid was split up into its components—oxygen and hydrogen—by the electric current. The discovery of the decomposition of metallic salt solutions, and of the easy separation of the metallic component, generally as a metallic coating upon one electrode, quickly followed. We find such depositions already technically employed at the end of the thirties. Jacobi, who is to be regarded as the founder of the art of electroplating, had already in 1839 prepared electrotypes of various objects, and these were

exhibited to the members of the St. Petersburg Academy. Other investigators must have also devoted themselves with zeal about this time to the study of the subject, for in 1840 and the following years a large number of methods were published relating to the preparation of solutions from which one could obtain, without fail, exceptionally beautiful deposits of certain metals. For example, in 1840 Ruolz, Elkington, and de la Rive proposed to use potassium cyanide solutions for obtaining deposits of gold and silver; in 1841 the same solution was proposed for copper and nickel, and a sodium hydrate solution for tin. Originally these methods were only designed to be used for electroplating purposes; but since very small amounts of metals can be deposited and detected in this way, similar methods were sought which should render feasible the quantitative estimation of metals, especially of poisonous ones in foods &c. (Bloxam, Morton). These methods are, for particular determinations, still in use. In 1805 Davy had pointed out incidentally in his working notes that the electric current might be used for chemical analysis, but it is Antoine Becquerel (the elder) who must be honoured as the real founder of analytical electro-chemistry. Becquerel published, as far back as 1830, a practical method for separating small amounts of lead and manganese from other metals, the manganese being obtained as peroxide at the anode. He showed, further, that it was possible in a definite time to separate as peroxide all the manganese contained in a known weight of manganese acetate. It was not, however, until the commencement of the sixties that electrolytic separations began to be used as aids to, and in some cases as substitutes for, the ordinary methods of analysis. In 1864 W. Gibbs separated electrolytically nickel and copper from nickel coins. In 1865 Luckow published a large number of experiments, and showed out of what solutions it was possible to obtain quantitative deposits of metals. In 1867 he received a

prize from the 'Mansfeld'schen Ober-Berg- und Hütten-Direktion' for his electrolytic method of estimating the copper contained in the Mansfeld schists.

Since this date the employment of electrolysis both for analytical and technical purposes has extended greatly. While the most important facts—e.g. the more or less good or rapid deposition of metals from different solutions, the variations in the current required, the separation of different elements or groups of elements from the same solution according to the current intensity or voltage, the influence of temperature, &c.—were long known, there was lacking, until a few years ago, a theory of electrolysis which explained clearly these phenomena.

Similarly there was no theory by means of which it was possible to explain clearly the changes in the energy-creating couple. It is true that at the commencement of this century a violent strife arose between the supporters of the 'contact theory' and the supporters of the 'chemical theory' of the origin of the energy in the voltaic cell. This strife continued into the third quarter of the century without the supporters of either the one theory or the other being enabled to give a clear explanation of the facts. Such an explanation has only become possible within the last few years, by aid of the theory of osmotic pressure, or 'osmosis.'

In the same way that this modern theory has satisfactorily explained the origin of the energy in the voltaic cell, the newer theories of solution and of electrolytic dissociation, which are the result of the researches carried on in the domain of physical chemistry during the past twenty years, have resulted in a deeper insight into the changes involved in the conduction of the current by electrolytes, and have elucidated many hitherto puzzling phenomena connected with this subject.

It will not therefore be superfluous if the opening chapters of this work be devoted to a brief summary of those currently accepted theories which are necessary for an

understanding of the phenomena to be observed in the conduct of electrolytic methods of analysis.¹

¹ Those interested in the study of the historical development of Electro-chemistry are referred to 'Elektrochemie, ihre Geschichte und Lehre,' by W. Ostwald.

PART I

THEORY OF ELECTROLYSIS

THE term 'electrolysis' is used to denote the chemical phenomena and changes, accompanied by movement of the particles of matter, which are produced when an electric current is passed through a fluid conductor, i.e. a conductor of the second class.

Faraday, with whom originated the terms still in use, named those bodies which, when in solution or in the molten state, conduct the current in this manner—'electrolytes.'

The term 'electrode' is used to denote those parts of the conductors of the first class, carrying the current to the electrolyte, which are in contact with it. A difference of potential is produced by the electric current at the electrodes, and as a result of this a movement of the ultimate particles of matter present in the electrolyte—the 'ions'—follows.

The particles, which differ fundamentally, move in different directions; those which move with the positive current are called 'kations,' whilst those moving in the contrary direction are called 'anions.' The electrode towards which the kations drift is called the 'kathode'; that towards which the anions drift is called the 'anode.'

The liberation of the ions at the electrodes causes changes at the latter, which vary greatly in character.

CHAPTER I

THE PHENOMENA OF ELECTROLYSIS

WHEN an electric current is passed through an electrolyte, movements of the ions of different kinds towards the opposite sides occur, and the products liberated at the electrodes are consequently different.

The most simple case for consideration is that in which the electrolyte, either in the dissolved or molten state, is made up of only two component parts, or contains only a base and an acid radical. For instance, if zinc or copper chloride be electrolysed with a sufficiently strong current, zinc or copper will be deposited at the kathode ; while the chlorine will drift towards the anode, and, when this is of a non-porous and to some extent chlorine-proof material (chlorine attacks and destroys in time all electrodes), will be liberated there as a gas. The same results are obtained if zinc chloride or lead chloride be melted in a crucible, or pipe-head of red clay previously warmed, and an electric current be passed through the mass, by means of a needle passing down the straight stem as kathode, and of a carbon pencil in the bowl as anode. Small spheres of molten zinc or lead collect at the bottom of the bowl, while a portion of the chlorine is liberated as gas at the anode. If hydrochloric acid be electrolysed with platinum electrodes, the ions are hydrogen and chlorine. The hydrogen drifts as the metals generally, towards the kathode ; and, being a gas, can be partly retained (occluded), according to the character of the electrode.

In the instances given above where the compounds have been made up of only two components, the products of the decomposition have been liberated directly at the electrodes. How will the results be affected when more complex compounds are electrolysed?

As a general rule the passage of the current is accompanied by a similar division into two sets of drifting ions, whether the constitution of the molecule be simple or complex.

Berzelius, who supposed that salts were made up of two parts—the base (an oxide) and the acid (an anhydride)—and consequently wrote the formula of potassium sulphate, for example, $K_2O.SO_3$, represented the school who thought that these two component parts not only acted as such in chemical reactions, but also drifted and separated as such in electrolysis. In order to bring this theory into harmony with the observed facts, he was obliged to assume, in addition, that the electric current decomposed water and liberated its constituent parts. The deposition of metals from neutral salt solutions was then explained by him as follows: The oxide of the metal drifted to the kathode, and was there reduced by the nascent hydrogen resulting from the decomposition of the water, and deposited as metal.

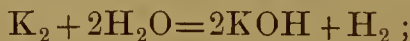
The halogen salts would not fit into this system, and it was partly on this account that he came to regard them as oxygen-holding compounds.

Daniell brushed away these contradictions, and proved that a salt is *in every case* to be regarded as a combination of a metal and an acid radical. The latter may be either a single element, as in the halogens, or a complex group of different elements.

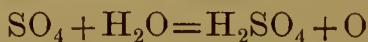
Hydrogen, on account of its behaviour, is to be regarded as a metal; the hydroxyl group of the different bases, on the contrary, is to be regarded as an acid radical. The acids are therefore hydrogen salts; the bases are salts, of which the acid radicals are the hydroxyl groups. Daniell further

showed that potassium sulphate, for example, on electrolysis between platinum electrodes, decomposes as other salts, into the metal ion K and the acid ion SO_4 . These component parts then lose their charges of electricity at the electrodes, and secondary action upon the water follows.¹

The potassium decomposes the water :



likewise the SO_4 ion at the anode :



The final products are therefore caustic potash and hydrogen at the kathode, an acid and oxygen at the anode. The amounts of alkali and acid formed at the electrodes are equivalent to the amounts of the respective gases.

That there is an actual formation of caustic potash solution at the one electrode, and of sulphuric acid at the other, is most simply shown by performing the electrolysis in a V-tube containing a litmus-coloured solution of the salt. The colour of the acid solution then changes to red, and of the alkali solution to blue. A similar proof that K and SO_4 are the products which drift towards the electrodes is obtained by covering some mercury contained in a vessel with potassium sulphate solution and by use of the mercury as kathode with a strong current. Potassium amalgam is formed, and this, separated from the electrolyte and treated with water, gives visible proof of the presence of potassium.

Water shares in the carrying of the current only to a very small degree.

The view held by Berzelius, that when potassium sulphate was electrolysed the water also suffered considerable decomposition, must be regarded as incorrect. Daniell himself proved this, by placing in the circuit a voltmeter containing dilute sulphuric acid, and noting that the volumes of gases liberated in both electrolytic cells

¹ The modern theory, as will be shown later, gives a simpler explanation of the still customary conception of secondary decomposition.

were the same. The electrolysis of dilute sulphuric acid, it is evident, must yield the same gases as that of potassium sulphate—namely, hydrogen and oxygen.

The electricity moves in such a way in conductors of the second class—i.e. electrolytes—that the metals, the metalloid radicals of salts and bases, and the hydrogen of the acids, all drift from the positive side of the cell-circuit towards the negative; while the acid radicals, the halogens, and the hydroxyl groups of the basic compounds drift in the contrary direction. No element or ion is known which can appear both as kation and anion. The following are to be classed as kations: The metals; hydrogen and the radical NH_4 ; organic substitution products of NH_4 , PH_4 , AsH_4 ; further, SR_3 , SeR_3 , TeR_3 , and other similar series in which R represents hydrocarbon radicals. The anions may be regarded as the remaining radicals of conducting bodies; as, for example, OH, Cl, Br, I, NO_2 , NO_3 , ClO_3 , ClO_4 , SO_4 , SeO_4 , PO_4 , AsO_4 .

In general, one may use the following definitions: The anion is all that which, combined with hydrogen or a metal, forms an electrolyte; the kation is all that which, combined with a halogen or an acid radical, forms an electrolyte. Oxygen, sulphur, selenium, and tellurium are anions, but they occur chiefly in the forms OH, SH, SeH, and TeH. The ions do not all possess the same valency; for instance, zinc is a dyad (Zn^{II}), bismuth a triad (Bi^{III}), while manganese and antimony are Mn^{II} and Sb^{III} respectively. The anions SO_4 and PO_4 are the first a dyad and the second a triad, and are written SO_4^{II} and PO_4^{III} . Metal ions and acid ions with variable valency are also known. The following list of metals, in which the valency is signified by the Roman numerals, shows examples of this: Fe^{II} , Fe^{III} ; Cu^{I} , Cu^{II} ; Hg^{I} , Hg^{II} ; Au^{I} , Au^{III} ; Sn^{II} , Sn^{IV} . Similarly the following variable anions are known: $\text{Fe}^{\text{III}}(\text{CN})_6$, $\text{Fe}^{\text{IV}}(\text{CN})_6$; $\text{Mn}^{\text{I}}\text{O}_4$, $\text{Mn}^{\text{II}}\text{O}_4$.

It has already been shown that one may regard both acids and bases as salts, and Hittorf has founded upon this

view the following general definition: *Electrolytes are salts*; they break up on electrolysis into the same atoms or atom groups which they exchange in chemical reactions. Later it was found that one could go further and say that all chemical reactions are exclusively reactions between ions—that is to say, elements or groups of elements can only be detected by the customary reagents when they are present in the ionic state. As an example of this we have the detection of Cl in common salt or in hydrochloric acid by means of silver nitrate.

In the chlorine substitution products of acetic acid, or in chloroform, no chlorine reaction is obtained with silver nitrate, for the ions of monochloroacetic acid are Na or H, and $\text{CH}_2\text{Cl.COO}$. The same reasoning applies to the test for iron in ferric chloride or sulphate of iron, as opposed to the test for iron in potassium ferrocyanide; for here also the splitting up into ions is different, and is as follows: $\text{Fe}_2|\text{Cl}_6$; $\text{Fe}|\text{SO}_4$; but $\text{K}_4|\text{Fe}(\text{CN})_6$.¹

When such salts as ferric chloride are electrolysed, the constituents which migrate as ions are found to be those which are detected by chemical reactions, and these separate at the electrodes. When, however, potassium ferrocyanide in which no iron can be detected by the ordinary tests, and in which therefore iron does not exist in the ionic state, is electrolysed, the complex group $\text{Fe}(\text{CN})_6$ migrates as a simple ion towards the anode, while no deposition of iron occurs at the kathode. Salts which contain two different bases are usually designated double salts.

The term strictly, however, ought to be confined to those salts which on electrolysis yield both the metallic constituents at the kathode; and salts of the class represented by potassium ferrocyanide, where the potassium alone migrates towards the kathode and the whole of the remaining complex group with the other metal migrates towards the anode, should be denoted by the term 'com-

¹ The bearing of these new views upon analytical chemistry is treated of in Ostwald's 'Theoretical Chemistry.'

plex.' (Further reference will be made to this point in Chapter VI., upon 'Dissociation of Salts in Solution.') The double salts of potassium cyanide, the double oxalates and phosphates, are examples of these complex salts. One may indeed regard these complex salts, owing to their method of splitting up, as binary salts, of which the anion is a complex acid radical. For example, we have potassium ferrocyanide, $K_4[Fe(CN)_6]$, the potassium salt of hydroferrocyanic acid; sodium platinum chloride, $Na_2[PtCl_6]$, the sodium salt of hydroplatinic acid; and, similarly, the cyanides $K_2 Ni(CN)_4$, $K Ag(CN)_2$, and the oxalate $K_3 Cr(C_2O_4)_3$.

It is noteworthy that, while potassium zinc sulphate, $K_2Zn(SO_4)_2$, is a true double salt, a complex salt potassium zincate is formed when caustic potash in excess is added to its solution. This salt is to be regarded as the potassium salt of zincic acid. Similar salts of bismuth, arsenic, and antimony are known.

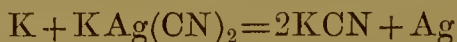
If the complex anion produced by electrolysis of these salts did not enter into secondary reactions, the separation of the metallic element would be as little possible by electrolysis as its detection by chemical reactions. In some cases these complex groups do indeed remain practically unchanged; in others they decompose by secondary reactions more or less quickly. In the case of a few, this decomposition is so rapid—as for example in the double cyanide of nickel and potassium—that one is inclined to regard them as true double salts. By such secondary decompositions of the anion, the metallic constituent of the group becomes an ion and migrates as a kation towards the kathode, where its deposition occurs. It may be remarked here that this kind of secondary deposition has become for many metals of practical importance, not only in chemical analysis, but also in electrotyping and electroplating.

From such solutions of complex salts it is possible to obtain even compact and adherent deposits of certain

metals which separate in crystalline or dendritic form, or which show a tendency towards formation of spongy deposits, when their simple salts are electrolysed. It is for this reason that silvering and gilding by 'the wet method'—that is to say, by electrolysis—are always undertaken by means of solutions of the double cyanides.

Hittorf has given the following detailed explanation of the electrolytic decomposition of the double cyanide of silver and potassium, when insoluble platinum electrodes similar to those used in electrolytic analyses are employed.

The kation potassium migrates towards the kathode; the remaining part of the molecule, $\text{Ag}(\text{CN})_2$, migrates as anion towards the anode, where it coats the surface of the platinum with AgCN , and (CN) is set free as gas. The migrating potassium anion, however, reacts secondarily with the undecomposed original salt, according to the equation



The liberated silver migrates towards the kathode, and is there deposited; the newly formed potassium cyanide re-dissolves the silver cyanide (AgCN) which covers the platinum anode, and forms anew the complex salt; and this cycle of changes continues until all the silver has been deposited at the kathode. An anode of silver is used when silver-plating; the anion $\text{Ag}(\text{CN})_2$ in this case dissolves an atom of silver from the anode surface, and re-forms with the 2KCN the complex salt $\text{KAg}(\text{CN})_2$.

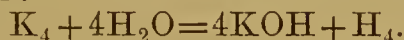
The decomposition of the double chloride of potassium and gold follows the same course.

The ions K and AuCl_4 are first formed; the anion AuCl_4 splits up into AuCl_3 and Cl , especially easily as the dilution increases; and this gold chloride (AuCl_3) then breaks up into its constituent elements, gold and chlorine.

If a solution of potassium ferrocyanide, $\text{K}_4\text{Fe}(\text{CN})_6$, slightly acidified with hydrochloric acid, be electrolysed between insoluble electrodes, Prussian blue, $(\text{Fe}_2)_2[\text{Fe}(\text{CN})_6]_3$,

is formed after some time, when the solution used is very dilute.

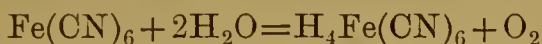
According to Hittorf, the potassium ion migrates towards the kathode and there decomposes water with liberation of hydrogen :



The radical $Fe(CN)_6$ drifts towards the anode, and in concentrated solutions—that is to say, in solutions containing sufficient potassium ferrocyanide—forms potassium ferricyanide :

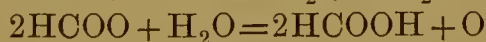
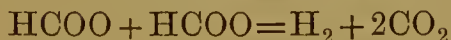


When, however, the solution is very dilute, the reaction takes a different course, and Prussian blue is formed according to the following equation :



When the anions are constituted of many elements, especially in the case of the radical groups of organic acids, one can frequently observe that reactions occur between the similarly constituted anions. These reactions result generally in the formation of gaseous products, which either escape or enter again into combination with other ions—simple or complex—present in the solution. Such reactions occur during the electrolysis of nearly all organic acids and salts.

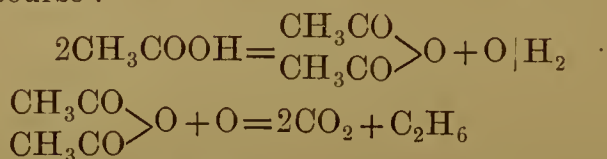
The decomposition of formic acid by electrolysis takes place according to the following equations :



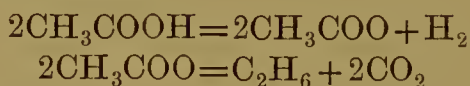
At the anode, carbon dioxide and oxygen are evolved, while hydrogen is evolved at the kathode. When the alkali salts of this acid are electrolysed, hydrogen is also evolved at the kathode in consequence of the reaction between the liberated alkali metal and the water. When

the formic acid salts of the heavy metals are electrolysed, the metal itself is of course deposited at the kathode.

The electrolysis of acetic acid or its salts follows a similar course :



or one may assume that a direct splitting up into the two anions CH_3COO occurs :

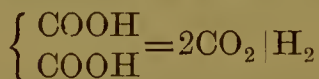


The final products at the anode are in either case ethane and carbon dioxide.

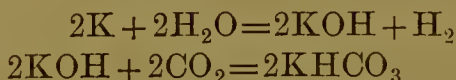
It is possible, however, for other products to occur, according to the concentration of the solution and the strength of the current.

Bourgoin found only carbon monoxide and carbon dioxide ; Bunsen found other products in addition to these ; while Jahn, when using a low-current density, found carbon dioxide and ethane.

When solutions of oxalic acid or its salts are decomposed by the electric current, the acid radical of the anion falls at once into two molecules of carbon dioxide.



If the potassium salt of this acid be electrolysed, the liberated carbon dioxide reacts with the potassium hydrate formed at the kathode, and potassium bicarbonate is formed :



When the electrolysis is performed with the ammonium salt, the corresponding ammonium compound is formed ; but this immediately splits up into ammonium hydrate and carbon dioxide.

From the heavy-metal salts the metals alone are deposited.

The salts of tartaric acid yield on electrolysis carbon dioxide, carbon monoxide, and oxygen as final products at the anode, with small quantities of formic aldehyd and formic acid.

The metal double salts of the above-named organic acids are occasionally made use of in electrolytic methods of analysis.

It is to be noted that only those organic compounds which correspond to the inorganic salts in constitution are to be regarded as true electrolytes.

CHAPTER II

FARADAY'S LAW

WHEN an electric current is passed through different bodies the movement of electricity in these bodies can occur in two different ways.

Conductors of the first class—metals, alloys, carbon, and a few other materials—exhibit a heating effect which follows the law of Joule ; but beyond this they exhibit no change. In the conductors of the second class—electrolytes—however, chemical change is a condition of the transfer of electricity.

In the previous chapter a large number of examples have been given of the chemical changes which accompany the passage of the electric current through molten or dissolved salts.

Michael Faraday, who was engaged with experiments bearing upon the measurement of electrical energy, discovered, as a result of these, in 1833, the law of 'invariable electrolytic action.' When any compound is decomposed by an electric current, the weight decomposed is found to be proportional to the amount of current used ; and the relative weights of the different elements or groups of elements separated in the same time are found to be represented by the equivalent weights of the elements.¹

Helmholtz expressed this law as follows :

The same current liberates in different electrolytes the

¹ The equivalent of an element is the atomic weight divided by the valency.

same number of valency bonds, or engages a like number in new combinations.

In general terms one may also express it thus : *All movement of electricity in an electrolyte is conditional upon simultaneous movement of the ions, and the connection between these is such that, with equal quantities of electricity, chemically equivalent amounts of the different ions must be in movement.*

The Law of Faraday thus makes no direct reference to the separation of the ions at the electrodes, but confines itself to the movement of electricity in the electrolyte. Faraday had himself already suggested that the conduction of the current, and separation of the products of the decomposition at the electrodes, were two distinct phenomena.

Nevertheless, the separation of the ions at the electrodes is the most convenient means by which to test the accuracy of Faraday's law.

This law has up to the present survived all the tests to which it has been submitted. If one connects in series in the same circuit, cells containing solutions of silver-nitrate, copper sulphate, and antimony chloride, the same quantity of electricity must pass through each cell, and by the law the weights of metals separated must be in the proportion of their equivalent weights—or $107.6 \text{ Ag} : \frac{63.3}{2} \text{ Cu} : \frac{119.6}{3} \text{ Sb}$.

The relative proportions of the acid radicals simultaneously separated at the anodes would be $\text{NO}_3 : \frac{\text{SO}_4}{2} : \frac{\text{Cl}_3}{3}$

For a practical illustration of this law Lüpke¹ recommends dilute sulphuric acid, potassium-silver cyanide, cuprous chloride solution acidified with hydrochloric acid, copper sulphate solution acidified with nitric acid, and a tin tetrachloride solution containing oxalate of ammonium.

¹ R. Lüpke, *Grundzüge der Elektrochemie auf experimenteller Basis*, Berlin, Springer. Also English translation of above by Pattison Muir.

Platinum foil is to be used as electrode material, or one may use for anode a strip of the metal the solution of which is to be electrolysed. A current obtained from 5 accumulators, which was allowed to pass through the cells for a period of 30 minutes, gave the following results :

	I		II		III		IV		V	
	H_2SO_4 1:12		$\text{KAg}(\text{CN})_2$		Cu_2Cl_2		CuSO_4		SnCl_4	
	—	+	—	+	—	+	—	+	—	+
Electrode material	Pt	Pt	Pt	Ag	Pt	Cu	Pt	Cu	Pt	Pt
Weight of deposited kations	67 c.c. H = 6.002 m.g.		650 m.g. Ag		380 m.g. Cu		190 m.g. Cu		170 m.g. Sn	
Ditto per 1 m.g. H.	1 m.g. H.		108.2 m.g. Ag		63.6 m.g. Cu		31.8 m.g. Cu		28.3 m.g. Sn	
Atomic weights	1		107.6		63.3		63.3		117.8	
Error per cent	—		+ .6		+ .4		+ .4		— .40	

These numbers enable one to obtain a very useful insight into the course of the electrolysis ; in II and III the metal ions, silver and copper, are univalent ; in IV the copper is divalent, and in V the tin is quadrivalent. Absolute accuracy is not to be expected in such experiments when complex electrolytes are used.

The use of the voltmeter, which will be described later, rests upon the absolute truth of this law, as confirmed by extended experiments, of the relative proportions of the deposited weights of metal or liberated volumes of gas.

In the following Table (p. 19) are given the electrochemical equivalents for those elements of chief importance to the electro-chemist. The weights given represent the amount separated or deposited by 1 ampère (= unit current intensity) during an interval of one second in m.grams, or during one hour in grams.

Since, as already pointed out, a known quantity of electricity occasions the movement or migration of equivalent weights of the different ions present in the electrolyte,

Element	Symbol	Valency	Atomic weight	Weight separated per ampère :	
				m.g. per second	gr. per hour
Aluminium .	Al	III	26·90	·093583	·3369
Antimony .	Sb	III	119·40	·415387	1·4953
Arsenic .	As	III	74·40	·258834	·9318
Bismuth .	Bi	III	206·40	·718055	2·5849
Cadmium .	Cd	II	111·30	·580811	2·0909
Chlorine .	Cl	I	35·19	·367273	1·3221
Cobalt .	Co	II	58·60	·305800	1·1008
Cobalt .	Co	III	58·60	·203866	·7339
Copper .	Cu	I	62·80	·655434	2·3595
Copper .	Cu	II	62·80	·327717	1·1797
Gold .	Au	III	195·70	·680830	2·4509
Hydrogen .	H	I	1·000	·0104368	·03757
Iron .	Fe	II	55·60	·290144	1·0445
Iron .	Fe	III	55·60	·193429	·6963
Lead .	Pb	II	205·40	1·082300	3·8962
Magnesium .	Mg	II	24·20	·126286	·4546
Manganese .	Mn	II	54·60	·284926	1·0257
Manganese .	Mn	III	54·60	·189950	·6838
Mercury .	Hg	I	198·90	2·075890	7·4732
Mercury .	Hg	II	198·90	1·037945	3·7366
Nickel .	Ni	II	58·60	·305800	1·1008
Nickel .	Ni	III	58·60	·203866	·7339
Oxygen .	O	II	15·88	·082868	·2983
Palladium .	Pd	II	104·70	·546369	1·9669
Platinum .	Pt	IV	193·30	·504361	1·8156
Potassium .	K	I	38·85	·405472	1·4596
Silver .	Ag	I	107·13	1·118100	4·0251
Sodium .	Na	I	22·87	·238691	·8592
Thallium .	Tl	II	202·64	1·057370	3·8065
Tin .	Sn	II	117·20	·611599	2·2017
Zinc .	Zn	II	65·00	·339197	1·2211

one may infer that a definite quantity of electricity moves with each equivalent of weight. Equivalent weights of the different ions have, that is to say, like capacities for electrical energy, and resemble in this the atomic masses of the elements, which, according to the law of Dulong and Petit, have like capacities for heat. Weber and Kohlrausch were the first who attempted to answer the question *How great is this quantity of electricity*, and to express in absolute units the electricity which is carried by 1 gram of hydrogen, or the equivalent weight of any element. The

researches of F. and W. Kohlrausch and of Lord Rayleigh have proved that this quantity is 96537 coulombs, the coulomb being the unit of electrical quantity. One coulomb therefore demands for its transport a mass of any ion represented by its equivalent weight expressed in grams, and multiplied by $\cdot 000010359$.

Faraday's law must not be interpreted to indicate that like quantities of electricity demand the expenditure of like amounts of work upon the different equivalents of matter. The law does not touch upon the work or energy ratios, but relates only to the one factor of electrical energy measurements—the quantity of current; the second factor—the pressure or potential—is unnoticed in this law.

In concluding this chapter it will be well to note briefly the units of electrical measurement. The unit of electrical energy is equal to 10^7 absolute units, and is called the *Joule*. The unit of potential, pressure, or electro-motive force is the *Volt*. The Latimer-Clark cell at 15°C . has an E.M.F. of 1.437 volts [the temperature correction is obtained by use of the formula $\cdot 0010(t-15)$], while the Daniell cell has an E.M.F. of about 1.1 volts.

The unit of electrical quantity is the *Coulomb*, which represents the quantity of electricity that by a fall of potential = 1 volt liberates 10^7 absolute units of energy.

If one coulomb pass any cross-section of the circuit in one second of time, the current is said to have a strength or intensity of 1 *Ampère*. The ampère is then the unit of current strength. If in any conductor a current of 1 ampère is produced by a fall of potential = 1 volt, the conductor possesses a resistance of 1 *Ohm*.

The standard resistance of 1 ohm is obtained by use at 0°C . of a column of mercury, 106.3 c.m. in length, and 1 sq. m.m. in sectional area.

CHAPTER III

THE CONSTITUTION OF THE ELECTROLYTE

THE conductors of the second class, the electrolytes, must necessarily be chemical compounds, since decomposition is a condition of current conduction.

The converse of this is not however equally true ; many compounds are known which do not conduct. This ability to act as conductors for the electric current is possessed generally by all substances in the molten state or in aqueous solution. No pure substance is however known, fluid at the ordinary temperature, that is a conductor to any marked degree. The pure acids—sulphuric acid, hydrochloric acid, &c.—which in aqueous solutions form some of the best conductors, are non-conductors. Organic compounds conduct only in the degree in which they possess the constitution and characteristics of true salts. The possibility of functioning as a conductor thus depends upon the ability to form from the molecules of the dissolved substance, particles of matter, which charged with positive or negative electricity are free to move in opposite directions. Since no substance in the molecular state can become charged with positive or negative electricity, one is obliged to assume that this property belongs exclusively to the parts of the molecule, the ions. The view that the electric current first causes a splitting up of the molecule, and then makes use of the sub-molecules for its transport, does not, however, correspond to the facts. Such a splitting up of the molecule would demand the expenditure of a definite amount of work. Clausius, therefore, in

1857 formulated the theory, that the current caused an acceleration of the molecular movements, and that the splitting up was a result of the collisions that ensued. The relative proportions of the numbers of molecules and sub-molecules remained at that time undetermined. It was not until 1887 that Arrhenius proved, from other characteristics of the electrolyte, that in solutions of salts, strong bases, and acids, these bodies are contained only in small part as such, and that they are for the most part split up into their respective ions. If the electric current were the cause of this ionisation of the substance, those chemical substances, the elements of which possessed the weakest chemical affinities, would be found to be the best conductors. Experiments, however, prove exactly the reverse. It may indeed be considered somewhat strange that it should be salts like potassium sulphate and sodium chloride, the elements of which have the strongest affinity for each other, that show the greatest ionisation when dissolved. This strangeness is, however, merely the result of a confusion of thought in regard to the stability, and the chemical activity of a substance.

The metals displace hydrogen with the greatest ease from its combinations in the mineral acids ; while in the hydro-carbons the hydrogen is unacted on by metals. The hydroxyl group in the alkaline hydrates is easily displaced by an acid radical ; in the alcohols the same group remains unattacked by acids. Thus it is the chemically inert bodies which show the strongest chemical affinities among their component elements. The chemically active bodies form on the other hand the best electrolytes, and the relationship between these two properties of compounds is so close that one can determine the conductivity by the chemical activity, and *vice versa*.

The theory that free ions exist in solutions may seem strange to those to whom it is new, for we are accustomed to associate with the free elements other properties than those noted in solutions.

For example, in a potassium chloride solution, which in the light of this theory contains chiefly potassium and chlorine as ions, one can observe neither the water-decomposing properties of the former, nor the characteristic smell of the latter.

The explanation of this is to be found in the fact that, although the free atoms of potassium and chlorine are present as ions in the solution, they carry extremely large charges of electricity, and on this account possess chemical properties differing widely from the normal ones. The energy charge of an ion is different from that of a free atom, and it is this that determines the different properties of the two. Let such a charged ion, as for example a potassium ion, deliver up its electrical charge at the electrode; the properties of the normal potassium atom at once reappear. The same is true of gaseous as well as of metallic ions, of anions as well as cations. From the above it follows, that when a metal salt is electrolysed and a deposition of the metal obtained at the kathode, the latter has occurred owing to the delivery of the electrical charges brought by the metal ions to the electrode; the now electrically neutral sub-molecules of the metal being thus able to manifest the usual metallic properties.

The acceptance of the theory, that the properties of an atom of an element may be entirely altered by the presence of an electric charge upon it, also explains the fact that isomeric ions of different valency possess different properties. The ferro- ion in divalent iron compounds, for example, exhibits different properties as regards colour and behaviour towards reagents, from those of the ferri- ion in ferric-salts.

A similar contrast is exhibited by the two groups $\text{Fe}(\text{CN})_6$ in yellow and red prussiate of potash; and the distinctive properties of the two MnO_4 ions in manganic and permanganic acids is another instance of the same kind. The differences in all these cases spring from differences in the charges of energy; the ions in each case carrying electric charges which vary as their valency.

CHAPTER IV

THE MIGRATION OF THE IONS

IN order to explain the fact that the passage of the electric current through acidified water caused a liberation of hydrogen and oxygen at the electrodes, different theories were put forward, even in the early days of the science. According to that advanced by Grotthüss (1805) the current made the one electrode positive, the other negative.

The electrodes then exerted a directive influence upon the polarised molecules of water, so that the oxygen side of the molecules faced the negative electrode, and the hydrogen side the positive. During electrolysis, only the two end molecules of each chain were decomposed, and the respective oxygen or hydrogen atoms set free; the remaining hydrogen and oxygen of these molecules united with the oxygen and hydrogen of the two neighbouring molecules, so that combination and decomposition alternated continuously in the electrolyte.

A definite electro-motive force was, according to this theory, necessary in order to start the decomposition, whereas experiment showed that solutions would conduct even with the feeblest currents.

Clausius pointed out this contradiction between fact and theory, and declared the theory to be untrustworthy. He ought to have been forced by this reasoning into a recognition of the absolute freedom of the ions in the electrolyte, but he saw only half the truth, and, as noted in the last chapter, advanced the view that the current does

not directly cause the breaking up of the molecule, but that by its action the loosely bound constituent atoms of the molecule are set in more rapid vibration and movement, and that, as a result of this, some molecules break up and the constituent parts of these migrate towards the electrodes. It was not until the year 1887 that Arrhenius published his *Dissociation Theory* and finally solved the problem.

Hittorf had, indeed, in the years 1853-1858 been engaged upon a study of the alterations in concentration of electrolytes at the electrodes, and had obtained in the course of this work a deep insight into the subject of the migration of the ions.

If the rate of migration of the two ions during electrolysis be the same, then the loss of the liquid around the two electrodes will be equal. This is, however, rarely the case, and Hittorf therefore concluded that the ions possess different velocities. Let one imagine an electrolyte, which contains an equal number of anions and cations (represented by the black and white circles in Fig. 1), divided in the middle by a porous partition (the vertical line in Fig. 1) so that equal numbers of anions

and cations are present on each side of it. The passage of the current will speedily disturb this equilibrium. In Fig. 1 the row (a) represents the electrolyte before the action of the electro-motive force; the row (b) repre-

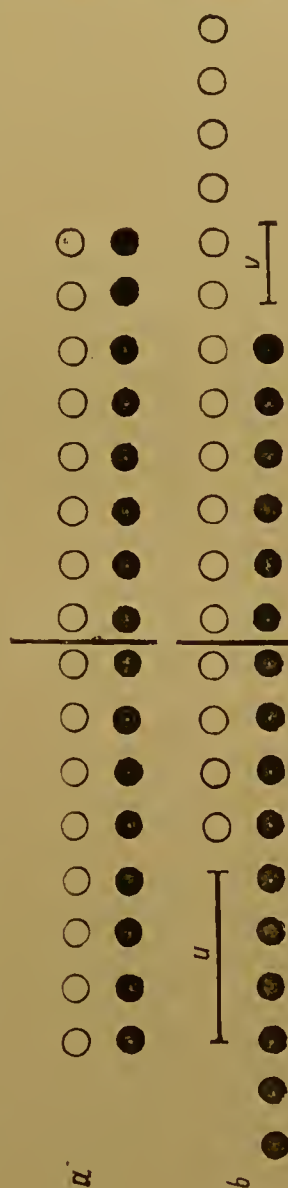


FIG. 1.—Migration of the Ions.

sents the same electrolyte after a migratory movement of the ions.

In this movement it has been assumed that the anions (the white circles) have moved twice as fast as the kations (the black circles), and the horizontal lines (u) and (v) represent the extent of the movement. Six ions have been liberated at each electrode ; consequently six equivalents of the electrolyte must have been decomposed and destroyed.

Four of these have been lost from the left-hand side of the partition, and the remaining two from the right-hand side ; in other words, these losses are in the ratio of the relative migration velocities of the anion and kation.

This system gives approximately a picture of the migration velocities of the ions of copper sulphate ; the SO_4 ion migrates nearly twice as fast as the Cu ion, and covers four units of space in the time that the Cu ion migrates through two. The quotients $2/6 = .33$ and $4/6 = .66$ are named by Hittorf the transport ratios for the concerned ions. This ratio, i.e. the relative velocities of migration, is quite independent of the working force ; the absolute velocities are on the contrary directly proportional to it. The temperature and concentration of the solution do not materially affect the figures.

As a result of these investigations Hittorf concluded, that in salts of which the double cyanide of silver and potassium $\text{KAg}(\text{CN})_2$ is a type, potassium is the positive ion and $\text{Ag}(\text{CN})_2$ the negative, and that these are the migrating ions ; while the separation of the silver from the anion is the result of a secondary reaction.

When a mixture of two salts is electrolysed, the ions, if they possess similar migration velocities, as for example chlorine and iodine, share the current in the proportion in which they are present in the mixed electrolyte ; the separation at the electrodes may however occur differently.

CHAPTER V

THE CONDUCTIVITY OF THE ELECTROLYTE

HITTORF had often given expression, in his papers upon the migration of the ions, to the opinion that a deeper knowledge of the real nature of electrolysis would be obtained by determinations of the specific conductivities of the different electrolytes. No reliable method of making such determinations was however known to him. The conductivity of a body is represented by the reciprocal of its resistance. For conductors of the first class, the resistance is dependent upon the form, the nature, and the temperature of the material used.

The unit of specific resistance is the ohm, or the resistance of a column of mercury 106.3 c.m. in length, and 1 sq. m.m. in sectional area at 0°C. (The Siemens unit of resistance, represented by a similar column 100 c.m. in length, is still occasionally used.) In connection with liquids, it is customary to speak of the conductivities rather than of the resistances, and to express these in the reciprocals of the ohm.

If one dissolves the molecular weight in grams of any salt in 1 litre of water, and brings this solution between two parallel electrode surfaces, placed at a fixed distance apart, the system will be found to possess a definite resistance in ohms, and corresponding to this a definite conductivity. These constants are named the molecular resistance, and the molecular conductivity. The molecular conductivity of an electrolyte increases with the tempera-

ture ; metallic conductors show the reverse phenomena. The molecular conductivity increases also with the dilution of the electrolyte ; but in this case the number of ions in the unit of volume, and therefore the specific conductivity of the electrolyte, is diminished. The maximum conductivity is therefore found at that point of dilution where the second effect commences to exceed the first.

In 1880 F. Kohlrausch published a useful method for determining the relative conductivities of electrolytes. The principle of this method consists in the use of the Wheatstone bridge with alternating currents in order to avoid the errors caused by polarisation ; a telephone is also used to replace the galvanometer.

The conductivities of liquids in comparison with the conductivities of the metals are very small. For example, such a good electrolyte as 20 per cent. hydrochloric acid solution at 18°C. possesses a conductivity only 71.4 millionths of that of mercury at 0°C. The fraction for 30 per cent. sulphuric acid is $\frac{69.1}{1,000,000}$, for 25 per cent. sodium chloride solution $\frac{20}{1,000,000}$, and for 10 per cent. copper sulphate solution it is only $\frac{3}{1,000,000}$.

The relative conductivities have also been determined for solutions which contain the equivalent weight of the salt in grams dissolved in one litre of water ; these are named the equivalent conductivities.¹

Kohlrausch found that the equivalent conductivities of the neutral salts were additively composed of two values, the one depending only on the anion, the other depending only on the kation.

¹ Further information upon conductivity can be obtained from the following works : *Lehrbuch der Allgemeinen Chemie*, vol. ii., by W. Ostwald ; *Theoretische Chemie*, by W. Nernst ; *Grundzüge der Elektrochemie auf experimenteller Basis*, by R. Lüpke ; *Elektrochemie*, by M. Le Blanc. The first-named most excellent book is that recommended for the study of the theoretical side of the subject.

These values represented in fact the relative migration velocities of the different ions.

Finally, the absolute values of the migration velocities of single ions have been determined.

These, with a potential drop of 1 volt per c.metre at 18°C., are as follows :—

Potassium ·00057 c.m. ; sodium ·00035 c.m. ; hydrogen ·00300 c.m. ; hydroxyl ·00157 c.m. ; ammonium ·00055 c.m. ; silver ·00046 c.m. ; chlorine ·00059 c.m. The ions of hydrogen and hydroxyl are therefore those which move most quickly.

CHAPTER VI

THE DISSOCIATION THEORY

VAN'T HOFF has shown in his theory of solution that Avogadro's law may be extended to dilute solutions, and that even the laws of gas volumes formulated by Boyle and Gay Lussac are still correct when applied to dilute salt solutions.

In other words, dissolved salts behave as gases. From the law of osmotic pressure Van't Hoff deduced other laws concerning the influence exerted by the dissolved salt upon the vapour pressure and the freezing point of the solvent. It was found, however, that all the acids, bases, and salts dissolved in water gave, when the normal molecular weights were accepted as correct, too high results for the osmotic pressure, vapour pressure, and freezing point determinations, or the molecular weights calculated from these results were too small. In 1887 S. Arrhenius gave the explanation of this discrepancy between the theoretical and observed results.

He had in an earlier paper upon the conductivity of electrolytes given expression to the view that two kinds of molecules—active and inactive—are present, and that part only of the active molecules conduct the current. The ratio of the active molecules to the total number of molecules present he named the coefficient of activity.

The comparison of the properties of the electrolyte as regards the depression of its freezing point, and its ability to conduct the electric current, led him to formulate the

theory—so fruitful in its after results—of the dissociation of all bodies dissolved in water. The discrepancy in the freezing point determination was, in the light of this theory, seen to be caused by the splitting up of the salt into its two component parts on solution; these fragments, or dissociated parts, giving too high a value to the gram molecule. The degree of dissociation of a salt on solution, i.e., the number of decomposed molecules, as determined by the observation of the freezing point, was found to be in very fair agreement with the number calculated from the electrical conductivity.

Since only the decomposed molecules conduct, Arrhenius assumed that these sub-molecules or ions carried electrical charges, even in solutions which formed no part of an electric circuit.

According to this theory of Arrhenius, the electric current in passing through an electrolyte does not decompose the molecules; these are already present—charged with their respective electric charges—in the ionic state.

Inversely, the conduction of the current by an electrolyte is dependent upon the presence of free ions; those molecules which have not undergone dissociation take no part in the electrolysis. The activity of the sub-molecules does not depend alone upon their conductivity, but, as already remarked, upon the chemical affinity of the molecule. When one dilutes an electrolyte with water, the conductivity increases up to a certain point; at and beyond this point of dilution, all the molecules are to be regarded as in the dissociated state. Anhydrous liquids, such as 100 per cent. sulphuric acid, and concentrated hydrochloric acid, &c., &c., do not conduct, because no dissociated molecules are present. Chemically pure water is also a non-electrolyte; the specific resistance at 18°C. being 24.75×10^{10} mercury units, or, expressed in another way, $1\frac{1}{2}$ million litres of water contain only 1 g. hydrogen, and 17 g. hydroxyl as ions.

It is noteworthy, therefore, that good conducting

liquids are formed by the solution of acids, bases, and salts in water. One is obliged to assume that water possesses in a peculiar degree the property of producing dissociation effects ; for the water molecules remain in these salt solutions practically unchanged, and do not share in the conduction of the current. Molten bodies act as electrolytes ; in this case dissociation would appear to be an effect of the increase of heat.

The fact that the ions possess charges of energy, differing from those of the corresponding atoms, and as a result of this possess different chemical properties, has already received mention in Chapter III (p. 23).

Whence comes then this property of water to effect dissociation ? One may perhaps assume that since solution is generally attended by a depression in temperature, there is an absorption of energy from without, which has some connection with the dissociation of the salt. Up to the present, however, no satisfactory explanation has been given as regards the origin of the electric charges carried by the separate ions. Ionisation is certain to cause some conversion into other forms, of the original energy of the atoms.

CHAPTER VII

THE CHEMICAL AND MOLECULAR CHANGES DURING
ELECTROLYSIS

ELECTROLYSIS is conditional upon the passage of measurable quantities of electricity into the electrolyte by its boundary surfaces.

This occasions a movement of electricity through the electrolyte, which is intimately connected with the movement of the ions. The current causes the anions to drift towards the anode, and the kations towards the kathode.

An accumulation of negative electricity at the anode and of positive electricity at the kathode results, which would speedily lead to a cessation of the current if this excess of electricity and accumulation of ions at the two electrodes were not destroyed. At the kathode positive electricity is drawn from the kations ; at the anode negative electricity is abstracted from the anions : and this withdrawal of the charges from the ions is followed by their change into neutral bodies. Electrolysis, strictly considered, therefore occurs in the voltaic cell. Of the ions which have delivered up their electric charges, only the metals can exist as such, and these are to be regarded therefore as primary products of the electrolysis. All non-metallic ions have but a short existence, and the substances which form at the electrodes are transformation products of ions which have lost their electric charges, i.e. secondary products. Examples of these are the molecular gases—chlorine, Cl_2 , hydrogen, H_2 , &c. &c.

The expenditure of work in effecting electrolysis is not, as already explained, required to split up into ions the molecules in the electrolyte, but is needed in order to effect the liberation of the charges of electricity from the ions at the electrodes. The amount of work demanded for this cannot be calculated from the heats of combination of the individual ions, but it is as a general rule proportional to the sum of these.

It has been customary to distinguish between the primary and secondary phenomena of electrolysis. Ostwald rightly points out, that it is neither advantageous nor logical to maintain this distinction longer. The electrolysis of potassium sulphate (see Chapter I) yields hydrogen and potassium hydrate at the kathode, oxygen and sulphuric acid at the anode. If now the separation of the oxygen and hydrogen at the two electrodes be regarded as a secondary phenomena, and if one assumes that, first of all, the ions of the salt—K and SO_4 —have actually separated but have immediately reacted with the surrounding water, one is met by the difficulty that a correspondingly higher electro-motive force would be required to effect the decomposition of this compound. Hydrogen and oxygen could not, if this assumption be correct, be liberated at a lower E.M.F. Observation has, however, shown that these gases are liberated with a much lower E.M.F. than that postulated. The expenditure of electro-motive force corresponds, then, not to those reactions or products which we have been in the habit of calling primary, but to the final products of the electrolysis.

It is, however, necessary to distinguish between those products which conduct the current and those which separate at the electrodes. Only in few cases are these one and the same, as for example in the fused chlorides—lead chloride and magnesium chloride.

In most cases the ions are unable to pass into the neutral state as regards electrical charge without undergoing an alteration in their chemical constitution. When

different substances are present, the separation is determined by the electro-motive force necessary to effect it ; those compounds which demand the least E.M.F. for their separation will be first obtained, this result being entirely independent of their classification, according to the older views, as primary or secondary products.

When the solution to be electrolysed is a mixture of various electrolytes, the proportion in which the different ions share in the conduction of the current is governed by two factors, the relative numbers of the different ions and their migration velocities. This compound expression is altered, however, when one comes to consider the separation of the single ions, since the different ions do not give up their charges of electricity with equal readiness.

With a slowly increasing electro-motive force, those ions which relinquish their charges most easily are the first to experience the change. For example, in a solution containing chloride and iodide of potassium, chlorine and iodine as ions arrive at the anode in exactly equal proportions, on account of the equality of their migration velocities (the anode must be of a material that is not attacked by these gases) ; but only iodine is separated at first. If one increases the E.M.F. a point is reached at which chlorine is also liberated ; this is about .35 volt higher than the first. Similar considerations regulate the deposition of metals from mixed solutions. The order in which they are deposited is as follows : Gold, platinum, palladium, silver, mercury, copper, hydrogen, lead, nickel, cobalt, iron, thallium, cadmium, zinc, manganese, aluminium, magnesium. Gold and platinum are most easily deposited, while zinc and aluminium are the most difficult to deposit of the better-known metals. The metals of the alkaline earths and the alkali metals can only be obtained as metals under especial conditions, and by use of a mercury kathode. The order of the above list corresponds to that of Volta's series, but it is dependent upon the electrolyte.

A clear view of this subject of the progressive deposition

of the metals is most easily obtained, by assuming that every ion possesses a definite and fixed force which tends to keep it in the ionic state ; and that this force can be measured and expressed in terms of the E.M.F., which is necessary to effect a separation of the ion, i.e. its transformation into the neutral condition.

It is for this reason that iodine can be separated more easily than bromine, and the latter more easily than chlorine ; and the same reasoning explains the ordering of the metals in the series already given. It is seen from this series that the noble metals and those allied to them have a distinct tendency to pass out of the ionic state ; whilst those at the other end of the series have the opposite tendency, and are always striving to enter into it. Hydrogen occupies a position midway between these two extremes.

The order in which the metals are deposited with a slowly increasing E.M.F. varies with the nature of the salt used for the electrolysis. For example, if an excess of potassium hydrate be added to a solution of the neutral salts of zinc or tin, an increase of from $\cdot 5$ to $\cdot 7$ volt is necessary in the E.M.F. required to effect deposition as compared with that required for the neutral solutions. The explanation of this lies in the fact that these metals form respectively zincate and stannate when excess of potassium hydrate is added to solutions of their neutral salts, and that these complex salts yield the zinc or tin as anion when electrolysed ;¹ while only very small amounts of zinc and tin are present as metals in the ionic state. Other examples of this kind are the solutions of the double oxalates and the double cyanides, which are so frequently used for electrolysis.

If then one has a liquid containing two or more metallic salts in solution, it ought to be possible, in view of the above facts, to deposit the single metals one after the other by the use of an extremely feeble current, which is gradually increased by means of a higher E.M.F. ; that

¹ Cf. Chap. I. p. 12.

is to say, an analytical separation of the metals by electrolytic methods should be practicable.

Freudenberg¹ has proved that this is possible for a considerable number of the metals.

If the current be increased before the whole of the more easily separated metal has been deposited, the second metal will take part in the deposition, and the limit will ultimately be attained at which the two metals arrive at the electrode, and are separated, in the ratio expressed by their relative migration velocities. A practical application of this phenomena occurs in the electroplating industry, when articles are coated with brass (copper and zinc). With feeble currents, copper alone is deposited. In order to obtain mixed metallic deposits of the required composition, it is necessary to pay careful attention to the nature and quantity of the salts used, and to the current density employed. An experiment illustrative of this deposition of alloys of the metals may be easily performed as follows :

A mixed solution of the sulphates of copper and iron (ferro-salt) containing a little sulphuric acid is electrolysed. With the electrodes a certain distance apart, copper alone is deposited at the kathode ; but if they be gradually moved nearer to each other the resistance of the electrolyte is reduced, the current density is increased, and a white alloy of copper and iron is deposited if the conditions be exactly right, or a black spongy deposit may be obtained.

The term 'current density' is used to denote the current strength or intensity divided by the area of the immersed part of the electrode.

The unit of area generally used for electrolytic separations in the chemical laboratory is the square decimetre ($= 100$ sq. centimetres $= .107642$ sq. foot). Current densities expressed in terms of this unit are denoted as 'normal densities,' and are generally written in this form : 'N.D. 100.'

The expression ' $\text{N.D. } 100 = 1.5 \text{ A}$ ' thus signifies that

¹ *Zeitsch. f. phys. Chemie*, 1893, 12, 197.

1.5 ampères of current is used for each 100 sq. centimetres of the electrode surface. For technical purposes the square metre ($= 10.76$ sq. feet) is used as unit of area. [In the calculations of current density, for technical purposes it is necessary to note carefully whether one or both surfaces of the electrodes will take part in the electrolysis. As a rule, more than two electrodes are used in each vat, and thus both surfaces of anode or kathode come into play.—*Translator's note.*]

It is evident from the foregoing consideration that the maintenance of a fixed current density is of great importance. The influence which the current density exerts is manifested in two directions, both the nature of the product and the quality of the deposit being dependent upon it. The latter influence is especially noticeable in the electrolysis of metallic salt solutions. As an example of the former, the statement that, according to the current density employed, either copper or cuprous chloride may be obtained on electrolysing a cupric chloride solution is to be noted. Palladium and molybdenum are obtained either as metals, as oxides, or there may be no deposit at all, according to the current density used for the electrolysis of their salts.

Again, sulphuric acid can be made to yield hydrogen peroxide, ozone, or persulphuric acid under similar variations of current density.

This influence of the current density is, however, best illustrated by the classical example of the decomposition of chromic chloride, as performed by Bunsen. According to the current density, one can obtain hydrogen, chromium trioxide, chromium sesquioxide, or metallic chromium. In order to obtain the last, the concentration of the solution must receive attention, as it has considerable influence upon the result.

Since the molecules of water are dissociated to such a slight extent, one can in most cases neglect the part played in the electrolysis by the ions of the water; for the limit

is quickly reached (even by very small current densities) at which their share in the procedure ceases. Thus, if the few hydrogen ions present in the water be caused by the current to drift towards the kathode, a definite time must always elapse before the original ratio between the numbers of dissociated and non-dissociated molecules is restored, i.e. before a further number of hydrogen ions have come into existence.

During this intervening time the current is compelled to make use of other kations in order to effect its passage through the electrolyte. For example, in the electrolysis of solutions of zinc chloride, hydrogen is liberated at the kathode when a feeble current is employed, and $\text{Zn}(\text{OH})_2$ is formed; but a slight increase in current strength is sufficient to cause the deposition of metallic zinc to become the chief effect of the electrolysis. Since in this case the question is merely one of the relative proportions of the zinc and hydrogen ions, it is evident that a better deposition of zinc will be obtained by use of a concentrated solution than by use of a more dilute one.

These considerations will also explain why, when different metallic salt solutions are electrolysed by means of insoluble electrodes, the last traces of the metal are always most troublesome to remove from the electrolyte. It is customary to surmount this difficulty by increasing the current density.

Bunsen even succeeded, by the use of very high current densities and hot saturated solutions, in obtaining smooth metallic deposits from the chloride salts of calcium, barium, and strontium. He, however, used an amalgamated platinum wire as kathode, the perfectly smooth surface of such a kathode being especially fitted to lessen the evolution of hydrogen.

Another well-known phenomena of electrolysis is also explained by the above considerations.

If one acidifies moderately strongly a neutral salt solution of nickel, cobalt, cadmium, or zinc, with a mineral

acid (3 percent. to 5 percent. by volume is generally sufficient), no deposition of metal occurs when the usual current density (100 N.D.=1 to 2 A) is employed, but an evolution of hydrogen gas takes place at the kathode. The mineral acids, when dissolved in water, undergo strong dissociation, and thus hydrogen ions are present in such solutions in great abundance ; the discharge potential of these hydrogen ions is also much below that of the ions of zinc, cadmium, &c., so that at the current density named it is impossible to exhaust the crowds of hydrogen ions and to bring the other metallic ions to the point of separation.

If, however, one electrolyses an acidified copper sulphate solution, the reverse of this occurs : copper will be deposited, whilst the hydrogen, under similar conditions to those obtaining above, will scarcely be visible. Hydrogen gas will only be liberated in quantity when the current density has been largely increased and the velocity of the copper ions no longer suffices to carry the whole of the current. This behaviour of different metals in acidified solutions of their salts is made the basis of an electrolytic method of separation for the so-called ' noble metals '—i.e. those standing above hydrogen in the list (see p. 35)—from the ' base metals,' i.e. those placed below hydrogen.

This method can also be used for analytical separations : as, for instance, for the separation of copper and zinc in the analysis of brass, or for the separation of copper and nickel in mint-nickel.

The second phenomena that is closely connected with the current density is the influence exerted by the latter upon the character of the deposits obtained at the kathode. The formation of spongy deposits is directly caused by the use of unsuitable current densities.

These deposits differ from bright metallic deposits in their dull and dark appearance and in their non-adherent and frequently powdery nature. This latter characteristic makes it almost impossible to wash them with liquids without loss.

Such deposits are alone caused by the use of current densities unsuited to the solution which is undergoing electrolysis. Zinc gives by the electrolysis of different solutions, bright, coherent, bluish-white deposits ; but from very dilute zinc sulphate solutions spongy deposits are nearly always obtained, even when high current densities are employed.

One can assume that in this case the cause lies in the arrival of considerable numbers of hydrogen ions with the zinc ions at the kathode surface. The individual minute bubbles of hydrogen do not detach themselves instantaneously from the rather rough surface of the zinc coating on this kathode, but escape from time to time in small masses of bubbles, and so destroy the possibility of a perfectly smooth and regular deposition of the metal. With concentrated solutions, on the other hand, it is possible to obtain entirely satisfactory deposits with current densities of from .5 to 1.5 ampères.

Mylius and Fromm have carried out investigations upon the electrolytic separation of zinc, which have led them to the opinion that the spongy zinc always contains either zinc oxide or a basic zinc salt.

If this view be correct, then the chemical changes in the solution during electrolysis must include those already noted as occurring when zinc chloride solution is electrolysed by a very feeble current ; hydrogen and zinc hydrate, $\text{Zn}(\text{OH})_2$, separate at the kathode, and the latter is mechanically enclosed in the deposit of zinc.

The metals which possess especial tendencies to form spongy deposits are zinc, cadmium, silver, gold, and, to a still greater degree, bismuth. This latter metal is deposited in a black powdery form from all its solutions by almost every current density which it is possible to employ. Bright deposits of copper, cadmium, and zinc can be obtained, by the use of weak currents, from solutions of their salts to which ammonia and certain substances have been added. The spongy metallic deposits have a tendency

to enclose liquids and gases, so that such deposits are useless for analytical purposes.

Another form of deposit similarly useless, though not on account of its spongy nature, is obtained from certain solutions of some metallic salts when a high current density is employed. In place of a smooth adherent deposit, one obtains a separation of needle-like or foliated growths, which are quite as unfitted as the spongy deposits for correct weight determinations. Such deposits are especially striking when warm saturated stannous chloride solution, concentrated lead acetate solution, silver nitrate solution, and zinc chloride solution are electrolysed.

Two of these solutions are purposely used in order to form the so-called 'trees' of silver or lead.

Some metals—as, for example, silver, bismuth, lead, &c.—possess the characteristic of being deposited from certain solutions simultaneously as metal on the kathode, and as peroxide on the anode. It is possible, however, by choice of solution and maintenance of a low current density, to obtain a deposition on the one electrode only. The influence of the current density in this matter is shown by the example of the electrolysis of a silver nitrate solution containing some free nitric acid. If an anode of thick silver wire in spiral form be used, no peroxide formation is noticeable; but if this be exchanged for a jacket electrode possessing sharp edges of the same metal, a coating of black silver peroxide will be produced, especially at the edges of the jacket electrode, where the current density is always the greatest.

When hydrogen or hydroxyl ions are caused to migrate, these in many cases react with the electrolyte. Thus, during the electrolysis of nitric acid, not only hydrogen, but nitrous acid, nitrogen, and ammonium hydrate are formed.

The hydroxyl anions as a rule react mutually at the anode, to form non-dissociated water molecules and oxygen.

When sulphuric acid or chromic acid is electrolysed, different modifications of the anode reaction may occur.

The liberated oxygen either forms ozone, O_3 , by the condensation of three atoms into the space of two, or it combines with water to form hydrogen peroxide, H_2O_2 , or at a particular current density the migrating SO_4 ion undergoes polymerisation at the anode and yields persulphuric acid, S_2O_8 .

As a rule the oxygen liberated at the anode is not polymerised (e.g. in solutions containing free nitric acid), but reacts upon the dissolved salt with formation of peroxides, as in solutions of the salts of silver, bismuth, manganese, and lead.

According to the conditions obtaining during the electrolysis of these salt solutions, either a deposition of metal at the kathode with some peroxide formation at the anode occurs, or only the peroxide is produced. This latter form of deposition is used analytically in the case of those metal salt solutions, from which a quantitative separation of the metal in this form is possible. Lead and manganese are the chief examples of metals whose separation can be effected in this way.

When a current flows through an electrolytic cell or through a voltaic couple, changes take place both at the electrode surfaces and in the electrolyte ; after some time the current steadily diminishes, often to a very considerable degree. This phenomenon cannot be explained solely by the change in the concentration of the electrolyte ; for an alteration in the 'ion concentration,' represented by 1 : 10, would only cause a difference of .06 volt, and it is the change at the electrode surfaces which must be regarded as the chief cause of the diminution. The term 'polarisation' is used to denote this increased resistance of the cell, and consequent falling off of the current strength. If one allows a current to pass through an electrolyte for some time, using insoluble electrodes of platinum, gold, or carbon, and then disconnects the primary current, and joins the

electrodes by a metallic conductor, it will be found that a current is now passing between the two electrodes in an opposite direction to that used for the electrolysis. This observation is most easily made by including a galvanometer in the external part of the circuit. This second current is the so-called polarisation current.

If two platinum electrodes be dipped into a dilute sulphuric acid solution, and a current with pressure of at least 1.6 to 1.7 volt be passed through it, hydrogen will be liberated at the kathode and oxygen at the anode. The greater part of these liberated gases pass up the surfaces of the electrodes in small bubbles and escape; a certain portion of each is absorbed by the material of the electrodes. If the primary or polarising current be interrupted after some time, a system will then exist consisting of two platinum electrodes immersed in dilute sulphuric acid, the one charged with oxygen, the other with hydrogen, gas—i.e. a gas couple or battery will have been produced, the current of which will of course be contrary in direction to the primary current. The E.M.F. of such a system is about 1.07 volt at the normal atmospheric pressure; at the commencement it is, however, often somewhat higher, owing to excess pressure. The gases retained by the electrodes form ions again, and pass into the solution. Such polarisation currents are usually of brief duration; the gases disappear from the electrodes, and the equilibrium of the system is restored. If in place of hydrogen a metal such as zinc or copper be deposited at the kathode, the interruption of the primary current results in the formation of a system which yields a current corresponding to that obtained from a voltaic couple made up of the metals zinc and platinum, or copper and platinum, with the particular electrolyte.

In order to obtain a clearer insight into the cause of polarisation, one may make use of Le Blanc's conception of 'Haftintensität.' According to this theory every ion possesses a definite force tending to keep it in the ionic

state (cf. earlier portion of this chapter, p. 36). The ions may, however, possess either a positive or a negative 'Haftintensität.' The electric charges can only be withdrawn from the first by the expenditure of work; the second class of ions, as they pass from the ionic into the neutral state, produces electrical energy. To the former class belong magnesium, aluminium, zinc, cadmium, nickel, cobalt, and iron; to the latter, lead, hydrogen, copper, mercury, and silver.

The anions may be similarly classified. If, then, it is necessary to deposit zinc from its solution, the least force with which this can be effected must exceed that represented by the 'Haftintensität' of zinc.

The moment this compelling force ceases to act, the tendency of the deposited zinc to pass into the ionic state—i.e. to go into solution—again becomes manifest, and the conditions for the production of an electric current in the opposite direction exist. The primary current for the decomposition of a compound must therefore be at least equal in strength to the sum of the 'Haftintensität' forces which have to be overcome. It is customary to speak of this as the 'decomposition value' of the electrolyte. For solutions containing the same anion, it rises with the 'Haftintensität' of the kation. Thus, for example, for the sulphates—copper sulphate, sulphuric acid, ferrous sulphate, and zinc sulphate—the decomposition values rise in the order in which these compounds are named. Since sulphuric acid possesses a decomposition value = 1.6 volt, it follows that that of copper sulphate is below this, whilst that of the two other sulphates is above it.

Using this conception of 'Haftintensität' it is possible to present the process by which the metals are separated by a slowly increasing electro-motive force from a mixed electrolyte, in the following manner:

Those ions which possess the smallest 'Haftintensität' will be first and most easily changed into neutral bodies. The polarisation current will, however, grow in strength

as the 'Haftintensität' of the separated ions—i.e. of the neutral bodies formed from the ions—increases.

The value of the decomposition force for any compound can be approximately calculated from the heat of formation of the electrolyte. The E.M.F. necessary for the decomposition of the more common electrolytes ranges from .5 up to 4 volts ; and for the same metal, varies with the concentration of the solution and with the constitution of the salt.

Complex salts possess, as one would have expected, a somewhat higher decomposition value than the simple salts. The following figures for the decomposition values of normal solutions of various metallic salts and acids have been obtained experimentally by Le Blanc : ¹

Compound	Volts	Compound	Volts
ZnSO ₄	2.35	CdCl ₂	1.88
ZnBr ₂	1.80	CoSO ₄	1.92
NiSO ₄	2.09	CoCl ₂	1.78
NiCl ₂	1.85	HCl	1.31
Pb(NO ₃) ₂	1.52	H ₂ SO ₄	1.67
AgNO ₃	.70	HNO ₃	1.69
CuSO ₄	1.24	NaOH	1.69
Cd(NO ₃) ₂	1.98	NH ₃	1.74
CdSO ₄	2.03		

The following figures have been calculated from the heat-formation data :

Compound	Volts	Compound	Volts
HgCl ₂	1.30	SnCl ₂	1.76
HgNO ₃	1.04	SnCl ₄	1.70
Fe ₂ (SO ₄) ₃	1.62	MnSO ₄	2.60
FeSO ₄	2.02	MnCl ₂	2.77
AuCl ₃	.39	CuCl ₂	1.36
FeCl ₂	2.16		

The deposition of the metal upon the kathode only

¹ *Zeitschr. f. phys. Chemie*, 1891, 8, 299.

requires to continue a very short time, in order to give rise to the polarisation phenomenon ; for Oberbeck states that an extremely thin coating of the metal suffices to make an electrode function as though composed of the solid metal.

PART II

MEASURING AND REGULATING THE CURRENT

A. CURRENT MEASUREMENT

It is generally of great importance in electrolytic processes that the current density, and very frequently the E.M.F. of the current also, should be maintained within certain fixed limits (see Chapter VII, pp. 38, 39).

These conditions can only be fulfilled by direct measurement of the strength and the E.M.F. of the current employed. The methods and apparatus for effecting the measurements of these two quantities differ, so that it will be most convenient to consider them separately.

CHAPTER VIII

MEASUREMENT OF THE CURRENT STRENGTH

IN order to measure the current strength, different effects of the electric current may be employed. One can make use of the chemical or the magnetic effect produced by the passage of the current. In the former case the apparatus used is known as a 'voltameter,' and must not be confused with the 'voltmeter,' the instrument by which the E.M.F. is measured; in the latter case the various instruments are known as 'galvanometers' and 'ammeters.'

According to Faraday's law (see Chapter II, pp. 16, 17), like amounts of current cause, in equal periods of time, equivalent amounts of simple or complex ions to drift towards the electrodes.

Here the ions separate as neutral bodies, or cause the separation of an equivalent amount of some loosely combined body from the electrolyte. Simple electrolytes, the decomposition products of which are easily determined by weight or measurement, can be used directly for measuring the amount of current that has been passed through them. The electrolytes used for this purpose are solutions of silver nitrate, copper sulphate, or dilute sulphuric acid, and the voltameters formed with these three electrolytes are known as the silver, copper, and detonating gas voltameters respectively.

If one of these is to be used for measuring the amount of current which is passing through a given cell, the

apparatus is so arranged that the resistance, the voltameter, and the electrolytic cell follow each other in the order named in the primary current circuit.

The Silver Voltameter.—Since it is not possible for any complications to occur in the deposition of silver from a solution of silver nitrate, the results obtained by use of this apparatus are extremely accurate.

It is customary to use a platinum crucible or basin as cathode, and a silver rod as anode. It is advisable to envelop the latter in a small piece of linen,¹ in order to prevent any small particles of silver from falling into the crucible or basin. A neutral concentrated solution of silver nitrate is used as the electrolyte.

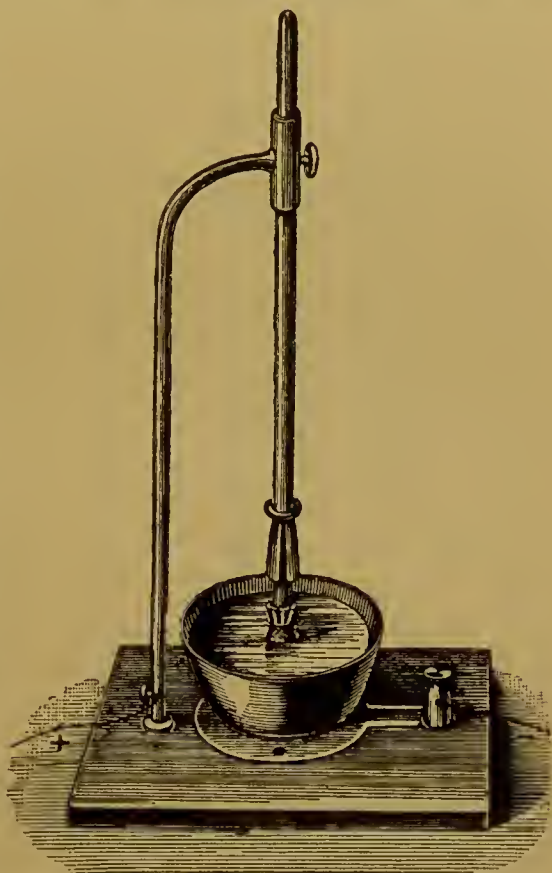


FIG. 2.—Silver Voltameter.

Fig. 2 is an illustration of the apparatus ready for use. Since silver shows a tendency, when strong currents are employed, to separate in single crystals, it is necessary when such currents have to be measured to use larger electrode surfaces, or to allow the current to pass through the voltameter for a very short time only.

¹ Care must be taken to employ linen quite free from organic or inorganic chemicals. Instances have occurred in which great trouble has been caused by the chemicals contained in the materials used for enveloping anodes. Cf. *Zeits. f. Elektrochem.* 4, 164.

Instead of the apparatus illustrated in fig. 2, it is of course possible to use a beaker containing the silver nitrate solution, with a platinum cone and silver strip as kathode and anode respectively. A current of 1 ampère in strength separates $\cdot 001118$ grm. silver per second, $\cdot 06708$ grm. per minute, and $4\cdot 025$ grms. per hour. After the circuit has been broken, the remaining electrolyte is poured out of the basin, or the cone is removed from the liquid, the electrode and its deposit of silver are washed with distilled water, then with alcohol, dried and weighed.

The Copper Voltameter.—The apparatus used is similar to that described above. Usually one employs two sheets of copper as electrodes, and a beaker for containing the copper sulphate solution. Oettel recommends the following composition for the electrolyte, in place of a concentrated solution of copper sulphate: 15 grms. copper sulphate, 5 grms. conc. sulphuric acid, 5 c.cm. alcohol, and 100 c.cm. water. This solution yields, with currents between $\cdot 06$ and $1\cdot 5$ ampère, results exactly concordant with those of the silver voltameter. With this solution the E.M.F. required lies between $\cdot 10$ and $\cdot 50$ volt, whereas double this E.M.F. is required with the more concentrated solution. 1 ampère separates $\cdot 01966$ grm. copper per minute and $1\cdot 1797$ grms. copper per hour.

The Detonating Gas Voltameter.—In this form of voltameter the current decomposes dilute sulphuric acid, and liberates hydrogen and oxygen at the two electrodes. The apparatus is so arranged that the volume of gas liberated at both the anode and kathode can be directly read off. The electrodes used are of platinum. The electrolyte is a solution of sulphuric acid of between $1\cdot 15$ and $1\cdot 20$ sp. gr. Many forms of this voltameter exist; one of the most convenient is that of Kohlrausch, illustrated in fig. 3. The graduated eudiometer tube contains a permanently fixed thermometer for determining the temperature of the contained gases; it is filled by simply reversing the position of the apparatus. Another form of

detonating gas voltameter is that of Walter Neumann (fig. 4). A movable levelling tube serves both for filling the eudiometer and for bringing the pressure under which the enclosed gas-volume is measured, exactly to that of the atmosphere. 1 ampère liberates 10.44 c.cms. detonating gas per minute if the measurement be made at 0°C . and 760 mm. pressure. Since the electrolytic dissociation of the



FIG. 3.—Kohlrausch's Detonating Gas Voltameter.

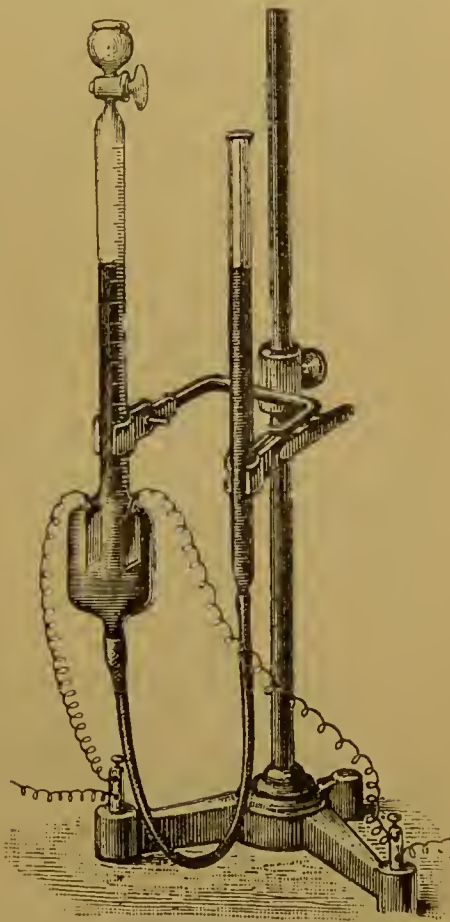


FIG. 4.—Neumann's Detonating Gas Voltameter.

electrolyte does not commence until an E.M.F. of 1.7 volt is employed under the most favourable conditions, and may require over 2 volts under some conditions of electrode surface and distance apart, the use of this voltameter is confined to those cases in which a moderately strong current is being used.

All the voltmeters described are faulty, except in very few instances, when used continuously for current measurements. They also appreciably increase the resistance of the circuit. On account of these drawbacks, they are seldom used in electrolytic work, and measuring instruments depending upon the electro-magnetic effects of the current are much more generally employed.

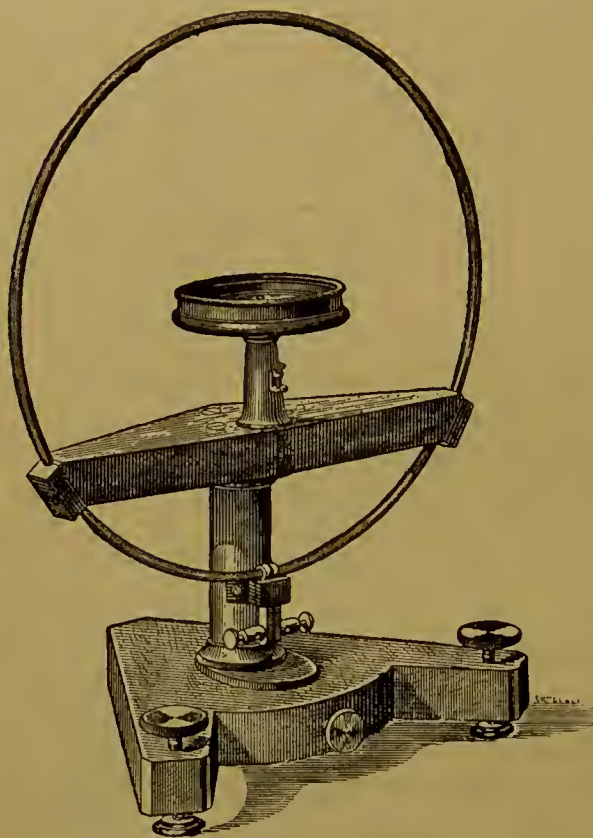


FIG. 5.—Tangent Galvanometer.

The Galvanometer.—A galvanometer is a measuring instrument, the mechanism of which depends upon the movements of a freely swinging magnetic needle under the action of the electric current. The simplest form—one which can be easily made by the student—is that known as the ‘tangent galvanometer’ (fig. 5).

A copper wire bent into a circle is placed with its plane vertical, and also in the magnetic meridian of the locality. At the centre of the hoop of copper wire a magnetic needle is placed, with opportunity for free movement in the horizontal plane. When at rest it will of course lie in the plane of the magnetic meridian. If the free ends of the copper wire be now connected with a cell, or other source of

current supply, the current will cause the needle to strive to place itself at right angles to the plane of the hoop. The force exerted by the current upon the needle is against that of the earth's magnetism, which seeks to hold the needle in its original north and south position. The needle will therefore be deviated by an angle that varies with the current strength, and it has been found that the tangent of this angle is directly proportional to the latter. The angular displacement of the needle in any galvanometer of this form is partly dependent upon the size of the instrument; and the calibration is best performed empirically by comparing these deviations with the current strength as ascertained by means of a voltameter placed in the same circuit. The current values are then written on the scale card of the galvanometer, so that a direct reading of the current strength is possible.

Since the angular deviation of the needle is inexact between 60° and 90° , it is necessary to place the instrument in a 'shunt circuit'—that is, a secondary circuit through which only a part of the primary current is passing—when strong currents have to be measured. If a conductor be divided at any point in the outer circuit, and two or more paths be opened to the current, a portion of it will pass along each of these. The relationship between these different portions of the main current is expressed by the reciprocals of the resistances of the separate wires. If the resistance of one wire be made ten times as great as that of the other, only one tenth of the current will pass along the first wire. It is thus possible to arrange for any desired fraction of the main current to pass through the galvanometer, by placing known resistances in the secondary circuit containing it.

Very delicate and sensitive instruments containing many coils of wire may be used in this manner for current measurements, as, for instance, the much-used horizontal galvanometer illustrated in fig. 6.

This galvanometer requires previous calibration by aid of a voltameter.

The Torsion Galvanometer.—The torsion galvanometer shown in fig. 7 is much used for measuring current strengths in electrolytic experimental work, and is both accurate and convenient. This galvanometer consists of a 'bell magnet' hung by a spiral spring between two 'multiplicators' containing a very large number of coils of wire. When the magnet has been forced from its original position by the action of a current passing through these coils, it can

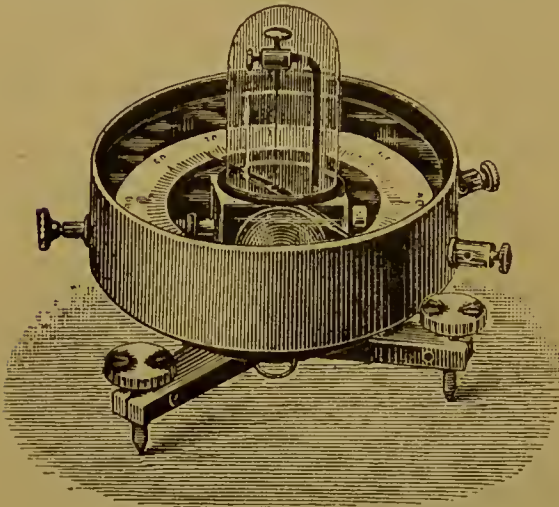


FIG. 6.—Horizontal Galvanometer.

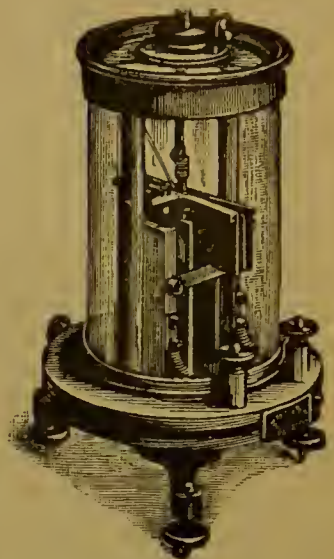


FIG. 7.—Torsion Galvanometer.

be brought back to its former position by turning the spiral spring.

The torsion of this spring—indicated by the circular angle through which the pointer attached to the upper part of the spring is moved in order to effect this—is proportional to the deviation of the magnet, and is therefore a measure of the strength of the passing current. The resistance of the wire coils of such a galvanometer is generally made to equal exactly 1 ohm, and each degree on the scale of angular measurement to equal $\cdot 001$ ampère. Since this degree of sensitiveness is generally much greater

than is necessary for technical purposes, and since the scale is only divided up to 180° , and the measurement of currents above $\cdot 17$ ampère is therefore impossible, it is customary to use shunt resistances made out of 'manganine'—equal to $\frac{1}{9}$, $\frac{1}{49}$, and $\frac{1}{99}$ ohm—with this galvanometer. One of these is inserted in the shunt circuit round the torsion galvanometer, and the fraction of the current in the main circuit which passes through the latter may therefore be reduced to $\frac{1}{10}$, $\frac{1}{50}$, or $\frac{1}{100}$ at will. Each degree of the scale by which the movement of the pointer is measured then indicates $\cdot 01$, $\cdot 05$, or $\cdot 10$ ampère, and the maximum current, the measurement of which is possible with these three different shunt resistances, is $1\cdot 7$, $8\cdot 5$, and 17 ampères respectively. Stronger currents than the latter may also be measured, by the application of the same principle with this form of galvanometer.

Ammeters for technical purposes.—Instruments have been constructed for technical use which permit currents of varying strength to be measured with sufficient accuracy; these have been named 'ampèremeters' or 'ammeters.'

The principle of the construction of these depends upon the observed fact that when a current is allowed to pass through a spiral of wire—a so-called solenoid—an attractive force will be exerted upon a short bar of soft iron

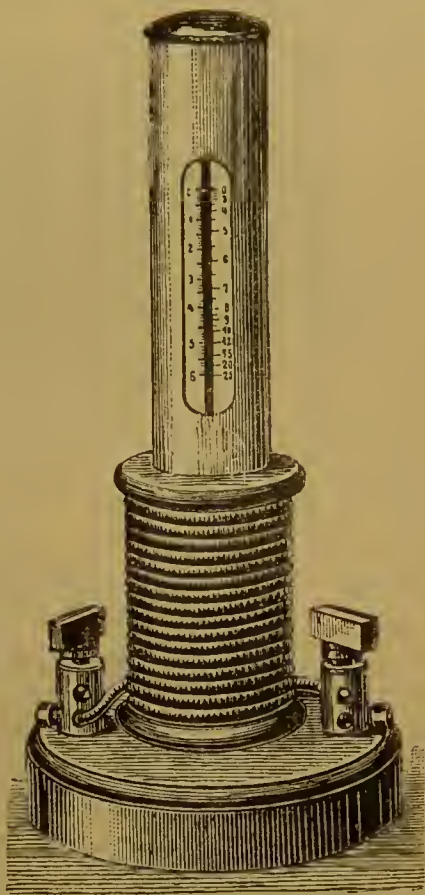


FIG. 8.—Kohlrausch's Spring Galvanometer.

placed near to one of its ends, or a force acting towards the periphery upon a piece of similar iron placed eccentrically

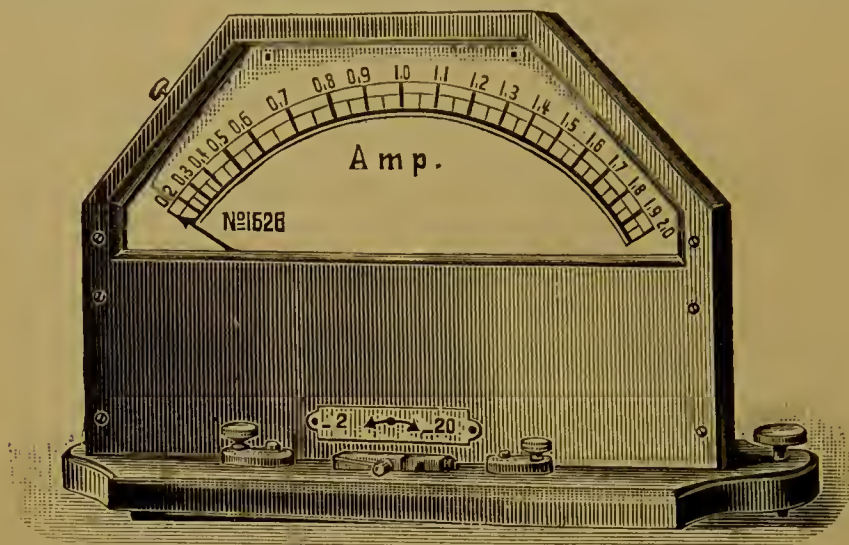


FIG. 9.—Ammeter.

within it. These instruments are calibrated empirically. They are sufficiently sensitive for ordinary work, but the divisions of the scale are usually very close together at the

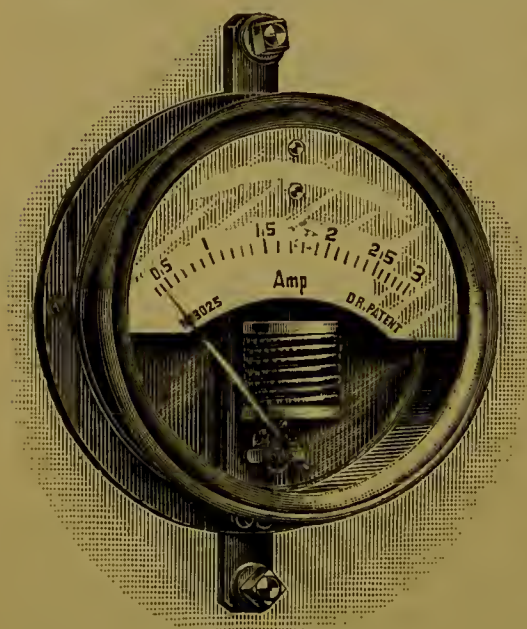


FIG. 10.—Ammeter.

lower part of the scale, so that accurate reading for weak currents is rendered somewhat difficult. The spring galvanometer designed by Kohlrausch (fig. 8) is of the type first described.

The current passing through a vertical solenoid causes it to draw within it a small cylinder of soft sheet iron suspended from a spiral spring. A pointer is attached to

the cylinder. The tension of the spring ultimately counter balances the attractive force exerted by the solenoid, and a position of equilibrium is attained.

The elongation of the spiral spring is indicated upon a scale by the pointer, and is a measure of the current strength. For electrolytic purposes, an instrument of this kind with a range of measurement of from $\cdot 50$ to $5\cdot 0$ ampères is sufficient. Two other forms of this type of ammeter are shown in figs. 9 and 10. In these the lineal

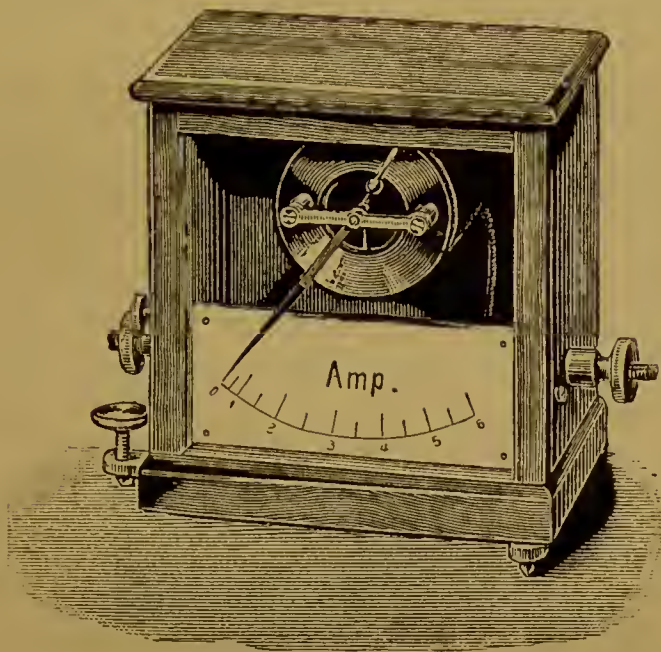


FIG. 11.—Ammeter.

movement of the iron cylinder within the solenoid is converted into the circular movement of the indicator pointer by means of a lever.

Other forms of ammeter are based upon the second action of solenoids noted above. These possess a horizontally placed solenoid, within which a short bar of soft iron—capable of movement about the axis of the solenoid—is set; one end of this bar being attached to a pointer moving over a circular scale (fig. 11).

When no current is passing, the counterpoise weight is

at the lowest point, and the index finger is at zero ; hence the name 'gravity control ammeters.'

When a current passes through the solenoid, the small bar of iron is attracted to the periphery of the coil. The stronger the current the greater is the displacement of the iron from its original position, until equilibrium is attained

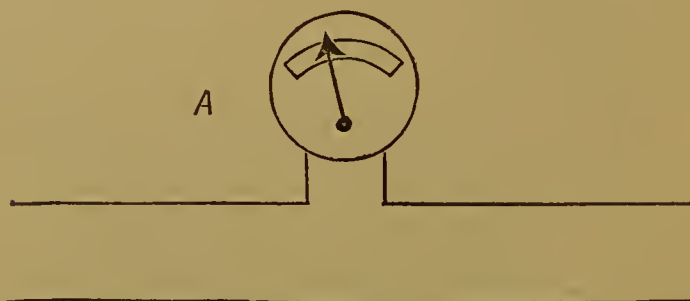


FIG. 12.—Current strength measurement.

between the rotary force exercised by the current, and the force of gravity.

It is necessary to note that all measurements of current strength are made by insertion of the measuring instrument

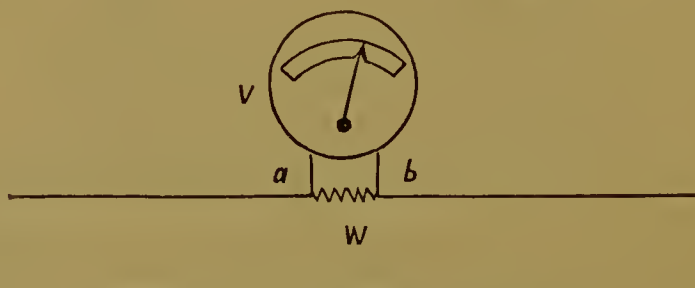


FIG. 13.—E.M.F. measurements.

in the main circuit, whereas measurements of E.M.F. are made by placing the instrument in a shunt circuit.

The diagrams (figs. 12 and 13) indicate the different arrangement in the two cases. A = an ammeter ; V = a voltmeter ; W = a resistance of known value.

CHAPTER IX

MEASUREMENT OF ELECTRO-MOTIVE FORCE (E.M.F.)

THE determination of the E.M.F. by the method of comparison with that of a standard cell is too inconvenient for technical use, which demands that the measurement should be easily and quickly made at any necessary place.

Instruments have therefore been designed for this purpose similar to those used for technical measurements of current strength. Galvanometers may even be directly used, under certain conditions, for carrying out measurements of E.M.F. If a conductor be divided into two or more distinct parts, the relative strength of currents in each of these is inversely proportional to the resistance. If one inserts a branch or loop circuit in the main circuit between any two points, a and b (see fig. 13), and places in this branch or shunt circuit a galvanometer of known resistance, the fraction of the main current passing through the galvanometer will be the smaller, the greater the resistance of the wire and galvanometer forming the shunt circuit. If the galvanometer be a high-resistance one, or if a high-resistance coil be inserted before it in the shunt circuit, it may be used directly for E.M.F. measurements.

According to Ohm's law, $1 \text{ ampère} \times 1 \text{ ohm} = 1 \text{ volt}$, and since the deviation of the needle of the galvanometer measures the former, and the resistance of the galvanometer and wire of the shunt circuit is known, it follows that the angular displacement of the needle is a

measure of the E.M.F., and that the scale of the galvanometer may be marked in volts. The torsion galvanometer illustrated in fig. 7 (see p. 56) is especially adapted for using in this way when inserted in a shunt circuit, with a suitable resistance coil in front of it. The internal resistance of the galvanometer is = 1 ohm, and the resistance box attached to this instrument contains resistances of 9, 99, and 999 ohms. The total resistance of the shunt circuit may thus be made equal to 1 ohm, 10, 100, or 1,000 ohms at will. If a deviation of the needle of 1° indicates a current of $\cdot 001$ ampère, it follows, from Ohm's law, that

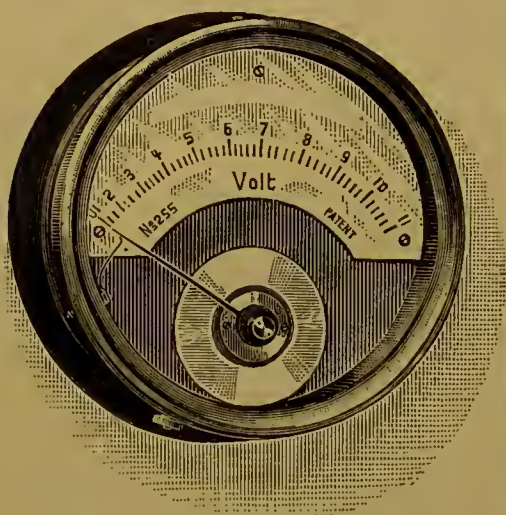


FIG. 14.—Voltmeter.

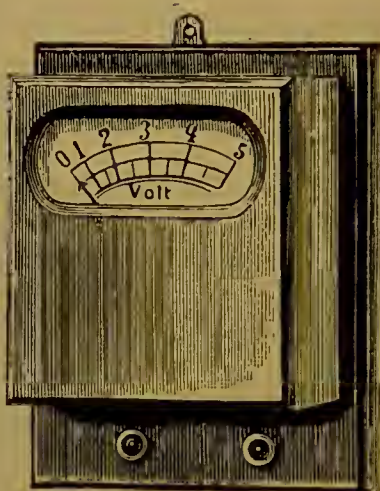


FIG. 15.—Voltmeter.

with the galvanometer alone in the shunt circuit, the E.M.F. represented by the deviation is $\cdot 001 \times 1 \cdot 0 = \cdot 001$ volt. If the resistance coils equal to 99 and 999 ohms be successively introduced into the shunt circuit, the total resistances will be raised to 100 and 1000 ohms, and 1° deviation will now equal $\cdot 001 \times 100 = \cdot 10$ volt or $\cdot 001 \times 1000 = 1 \cdot 0$ volt, according to the resistance used. It is therefore possible, with the aid of the three resistance coils named, to measure E.M.F.s lying between $\cdot 001$ and 17 volts by means of the torsion galvanometer. The galvanometer is connected with the wires of the shunt

circuit by means of its corresponding binding screws, the greatest resistance of the three attached to the galvanometer always being first put into the circuit with it in order to guard against the danger from excessive currents. When a suitable deviation of the needle has been obtained (in some cases the internal resistance of the galvanometer alone will suffice to keep the deviation within the limits required), the torsion screw is turned until the needle is again brought back to its original position, and the E.M.F. is calculated from the angular measurement given by the indicator finger of the torsion screw. In exactly the same manner as that in which the torsion galvanometer may be changed into a voltmeter, the different forms of technical ammeters may be converted into instruments for measuring E.M.F.s—by increase of their resistance. Technical voltmeters closely resemble ammeters in appearance, and differ in construction from these only in the greater number of coils which they possess, and in their higher resistance. Illustrations of some of the usual forms of voltmeter are given in figs. 14–16; others resemble in their outward form the ammeters of which illustrations appear on pp. 58, 59. Voltmeters must always be inserted in a shunt circuit (see fig. 13), and not in the main circuit.



FIG. 16.—Voltmeter.

B. REGULATING THE CURRENT

It is necessary now to turn to a consideration of the methods and apparatus by which the regulation of the current is effected. In Chapter VII the influence of the E.M.F and density of the electric current upon electrolytic phenomena in certain cases was discussed, and in Chapters VIII and IX the instruments by which these two electrical quantities are measured were described.

The question now arises—How must one proceed in order to obtain the required current and E.M.F. from the different sources of electrical energy, or how can one attain in the electrolytic cell the exact current conditions that are desired?

The answer to this question is obtained by a consideration of Ohm's law. The current strength or intensity depends, in the first place, upon the electro-motive force created by the source of electrical energy. The greater this force in any complete electrical circuit, the greater is the intensity of the current that will pass through the circuit under otherwise exactly equal conditions. All conductors—metallic and non-metallic, solid and fluid—offer, however, a definite resistance to the passage of the current, and the amount of current passing any given point in conductors of fixed sectional area in a unit of time—for example, 1 second—varies inversely to the resistance. The greater therefore the total resistance of any complete circuit, the smaller is the current which passes through it. From this it follows that the intensity or strength of the

current in any complete circuit is equal to the E.M.F. divided by the sum of the resistances which it contains. If one employs the usual units of current measurement (see Chapter II, p. 20), one may state this law in the following manner : $1 \text{ ampère} = \frac{1 \text{ volt}}{1 \text{ ohm}}$

Ohm's law therefore shows how it is possible to attain the desired current density, or current strength, in any electrolytic cell which offers a known resistance to the passage of the current, and for which it is necessary to use a definite E.M.F. to effect the electrolytic decomposition.

CHAPTER X

INCREASING THE CURRENT STRENGTH

It is possible to increase the current strength in any circuit by increasing the E.M.F., or, when feasible, by diminishing the total resistance of the circuit. A diminution of current strength is effected in the contrary manner—the E.M.F. is diminished or the resistance is increased. As regards the first, both methods are not always applicable. The increase of the E.M.F. has definite limits fixed by the type and construction of the source of energy employed. The dynamo produces an E.M.F. the upper limit of which is dependent upon the construction, and is speedily reached. The E.M.F. produced by the thermo-battery is likewise limited, and depends—apart from small variations—upon the heat applied and the size of the type used, that is, upon the number of single thermo-couples it contains. With galvanic batteries and accumulators the maximum E.M.F. that can be obtained is similarly fixed, in these cases being dependent upon the nature of the electrodes and of the electrolytes. In order to obtain from galvanic cells a greater E.M.F. than can be obtained from the single galvanic couple, a number of the single elements are connected together to form a battery. The manner in which the connections of single elements to form batteries are made is of importance. If the connecting or coupling—as, for example, of five Daniell elements—be so carried out that the copper of one cell is connected to the zinc of the next, the arrangement is called ‘series coupling,’ and is diagrammatically represented by fig. 17. The current in this case passes from the first through

the second, and so on, and the E.M.F. of the series is equal to five times that of a single Daniell cell. Each cell possesses, however, a definite internal resistance, and the total internal resistance of this

series will be five times that of the single cell. The current intensity is not increased in the slightest degree by this method of coupling cells together, for the current strength is practically the same with the five cells in series as with the single cell. If, however, the resistance of the external circuit is very large as compared with the internal resistance of the five cells forming the battery, the current strength obtained with the series arrangement of the cells will be nearly five times as great as it would have been with the single cell. In order to



FIG. 17.—Series Coupling of five Daniell Cells.

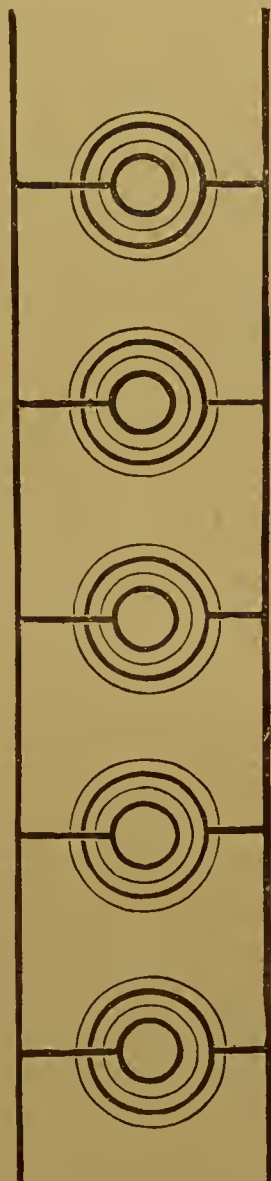


FIG. 18.—Parallel Coupling of five Daniell Cells.

obtain, therefore, large currents when the external resistance is great, the cells are coupled in series. The other arrangement of cell coupling is known as 'parallel coupling,' and is used when the resistance of the external circuit is

small. By this term is understood the arrangement in which similar poles of the successive cells are connected together. Fig. 18 shows this method of coupling applied to five Daniell cells. All the copper poles are connected together, likewise all the zinc poles; and the combined copper cylinders act as one large cylinder five times their size would behave if placed in the same electrolyte, opposite to an equally enlarged cylinder of zinc. The sectional area of the liquid between the electrodes is, by the 'parallel coupling' of the five cells, increased to five times that of the single cell, and the internal resistance of the five cells is thus reduced to one-fifth of that of any one of them alone. The current strength obtained by this 'parallel coupling' of the cells is therefore equal to the E.M.F. of a Daniell cell divided by one-fifth of the internal resistance of this form of primary cell. If the resistance of the external circuit be high, the current strength obtained will differ but slightly from that of a single Daniell cell; for in this case the E.M.F. of one Daniell element is divided by the whole external resistance. These considerations have led to the formation of the rule given above, that 'parallel coupling should be used only when the resistance of the external circuit is low.'

In carrying out the various electrolytic decompositions required in analytical chemistry, the resistance of the electrolytic cell will be found to vary between $\cdot 40$ and $2\cdot 5$ ohms, according to the nature and temperature of the electrolyte. The resistance of the conducting wire can be neglected. In those cases in which the resistance of the external part of the circuit including the electrolytic cell is approximately equal to the internal resistance of the primary cell, it will be found most advantageous to couple the cells both in series and in parallel, and the arrangement thus obtained is known as 'series parallel coupling.' Figs. 19 A, B, C, D are diagrammatic representations of this type of coupling, and are self-explanatory.

The arrangement shown in fig. 19 A gives an E.M.F. equal to two Daniell cells, with an internal resistance

equal to one half that of a single cell. The arrangements shown in figs. 19 B, c, and D yield E.M.F.s equal to two, three, and four times the E.M.F. of a single Daniell cell respectively ; while the internal resistance is equal to that of one Daniell cell in figs. 19 B and 19 c, and equal to that of two Daniell cells in the arrangement shown in fig. 19 D.

The choice of the coupling arrangement to be used in any particular case is governed by the resistance of the external portion of the circuit. As a general rule it will

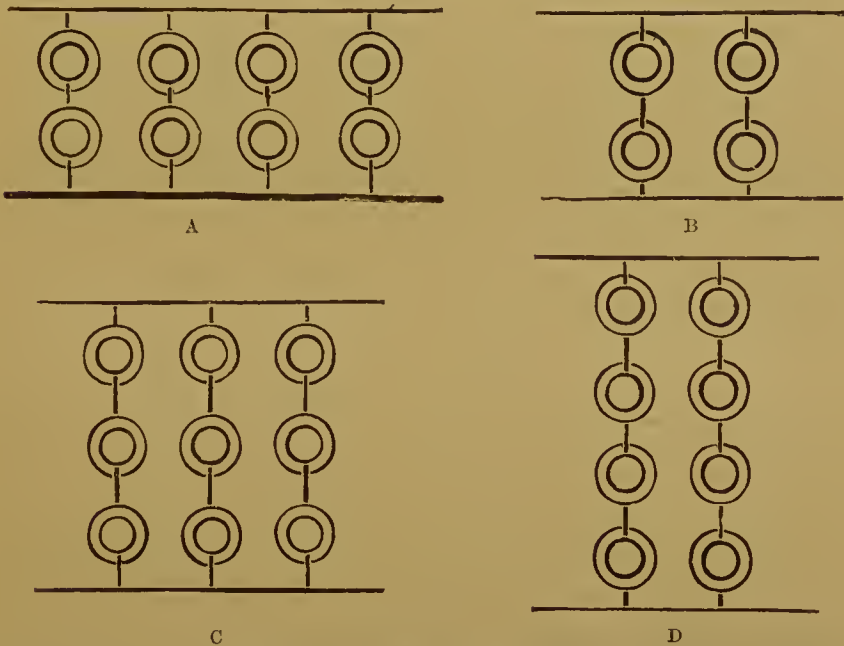


FIG. 19.—A, B, c, D, Diagrams illustrating 'Series Parallel Coupling.'

be found advisable to couple the cells in such a manner that the internal resistance of the battery is approximately equal to the total resistance of the external circuit. Secondary cells or accumulators are used in a similar manner to that just described for primary cells and batteries. In this case, however, the method of parallel coupling is in most instances unnecessary, since accumulators are very seldom used containing only single plates of spongy lead and lead peroxide. As a rule a secondary cell contains a large number of these positive and negative

plates arranged alternately. All the negative plates are connected together, and similarly all the positive plates. Such a secondary cell therefore represents, and acts as, a battery of single elements coupled in parallel.

It sometimes happens that many electrolytic decompositions have to be proceeded with simultaneously, and in such cases parallel coupling of the smaller types of accumulator may be necessary. For electrolytic purposes an E.M.F. of from 4 to 6 volts is usually sufficient. When accumulators are used as the source of electrical energy, three or four cells coupled in series are therefore required. If the only source of electrical energy for charging the accumulators be a thermo-battery, it is necessary to employ accumulator cells of the smaller pattern, and in the use of these for electrolytic separations cases can occur in which 'series parallel coupling' is necessary. It is most convenient in such cases to construct a special switchboard which for four accumulator cells would have the form shown in fig. 20. Small pieces of brass of the shapes shown in the diagrams of fig. 20 are screwed upon a base-board. Each of these is connected to the wire proceeding from a pole of an accumulator cell; the upper row of brass plates being connected to the positive, the lower row to the negative poles, in the order indicated by the numbers in the diagram. The round openings between the separate pieces of brass serve for the reception of accurately ground-in metal plugs, which complete the connection between neighbouring pieces, and consequently also between definite electrodes of the battery cells. The arrangement of the plugs in these openings makes it possible to couple the four cells in series or in parallel with the expenditure of a minimum amount of time and trouble.

In fig. 20 A the four cells are coupled in parallel, and the E.M.F. produced is only equal to 2 volts.

In the arrangement of the plugs shown in fig. 20 B, cells Nos. 1 and 2 and also cells Nos. 3 and 4 are coupled in parallel, but the plug in the middle serves to couple each of

these pairs in series, so that the total E.M.F. obtained is 4 volts. Fig. 20 c represents an arrangement by which an E.M.F. of 6 volts is obtained ; cells Nos. 1, 2, and 3 are coupled in series, Nos. 3 and 4 in parallel. This arrangement cannot be recommended for practical purposes, as the accumulator cells would be unequally discharged.

It is better that the discharge of the cells should occur equally, and that the recharging should likewise be regular, so that the recharging of the cells may be completed at one and the same time.

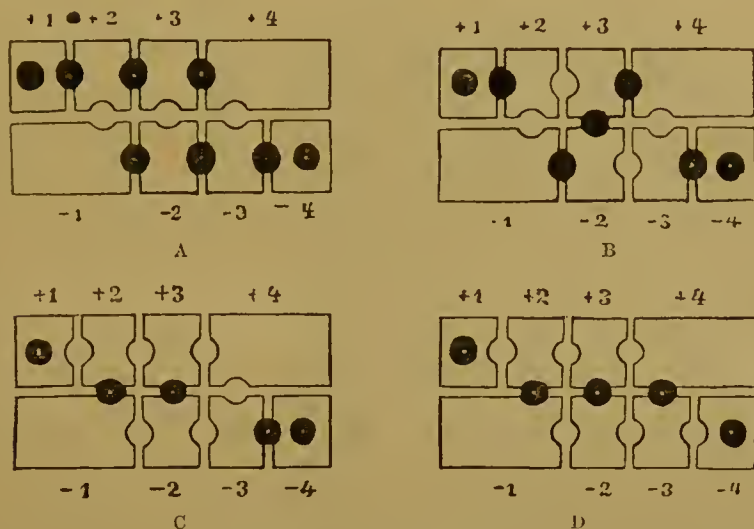


FIG. 20.—A, B, C, D, Diagrams of a Switchboard for Accumulators.

By the arrangement of the plugs shown in fig. 20 D all four cells are coupled in series. A useful form of accumulator battery of this kind is shown in fig. 21. The battery contains four accumulator cells, each of eight ampère hours' capacity. The charging can be effected by means of a thermo-battery. The four cells are enclosed in a wooden chest, upon which a switchboard similar to that described above is screwed.

When charging the cells by aid of a thermo-battery, it is necessary to adopt the parallel coupling shown in fig. 20 A. This switchboard may also be used for larger patterns of accumulator cells, if it be necessary to use these

in connection with one or two of the smaller cells. In order to effect this combination, holes are bored in the metal plates, and plugs are inserted which make the connection with the poles of the larger cell.

In the larger patterns of Gulcher's thermo-battery there are sixty-six thermal elements coupled in series. An alteration of the manner of coupling is in this case not possible, nor is it necessary in the majority of electrolytic separations ; for with an E.M.F. of 4 volts and a current strength of

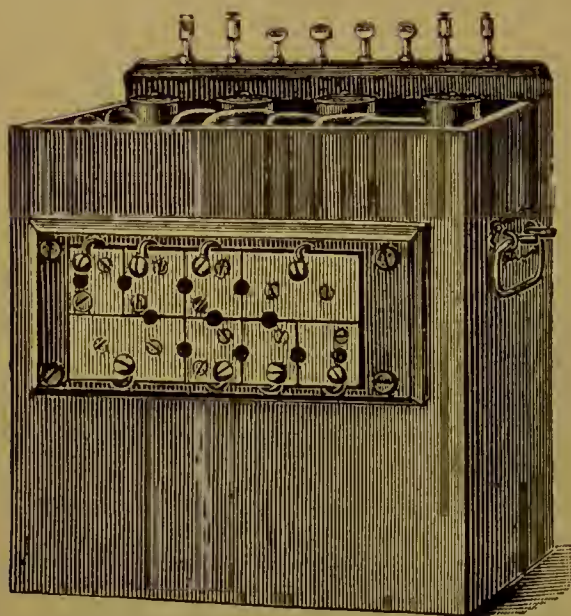


FIG. 21.—Accumulator Battery with Switch-board.

about 2 ampères (this varies according to the resistance), nearly all the electrolytic analyses can be carried out. The E.M.F. and with it the current strength obtained from such a thermo-battery can be diminished, if the wire connection be made not as customarily at the terminal binding screw, but at one of the cooling

plates attached to the negative elements. Should a case occur in which the E.M.F. or current strength yielded by the thermo-battery is insufficient to effect the desired electrolysis, one can use the thermo-battery and accumulators together, coupled in parallel or in series.¹

As already noted at the commencement of this chapter, a second method of increasing the current strength in any circuit is that dependent upon a decrease of the total resistance. This is made up of the internal resistance of

¹ Elbs, *Chem. Zeitg.* 1893, 17, 66, 97.

the source of electrical energy and of the resistance of the external circuit, the latter of which equals the resistance of the metallic and fluid conductors, and in addition that produced by polarisation.

The reduction of the internal resistance of the source of electrical energy is only feasible with galvanic elements. It is effected by coupling a large number of the cells in parallel—that is, by greatly increasing the superficial area of the electrodes.

In the case of accumulators—at least, as regards the larger patterns—this has already been carried out, and the internal resistance of these is extremely small. In the case of dynamos and thermo-batteries the internal resistance cannot be reduced at will in this manner. The resistance of the external circuit may be diminished in various ways. It is known that the resistance of the metallic conductors or ‘leads,’ apart from the specific resistance of the metal used, is directly proportional to their length, and inversely proportional to their sectional area. For copper wire conductors it is customary to allow 2 or 3 ampères per sq. mm. ; and since in electrolytic experiments currents of more than 2 ampères are comparatively rarely used, it follows that for this class of work copper wire 1 sq. mm. in sectional area is ample. The resistance offered by the electrolytic cell may be diminished, as in the case of the battery cell, by increase of the superficial area of the electrodes. A second method is to increase the conductivity of the electrolyte.¹ This method, in most cases of electrolytic deposition, cannot be made use of, since a definite composition and degree of concentration of the solution have to be maintained in order to effect the desired separations. As a general rule it is not advantageous in electrolytic analysis to utilise the electrical energy in the most economical manner.

¹ [In the majority of instances heating an electrolyte increases its conductivity, and this method of reducing the resistance of the electrolytic cell is very often used.—*Translator's note.*]

CHAPTER XI

REDUCING THE CURRENT STRENGTH

THE reduction of the current strength is of course effected by means exactly the reverse of those adopted in order to increase it. The reduction of the E.M.F. of the source of electrical energy cannot be effected in the case of primary or secondary cells ; and it is only in special cases—as, for example, in separations based upon the different ‘decomposition values’ of metallic salts—that need for a reduction of the E.M.F. exists. A reduced E.M.F. can be obtained from a thermo-battery when one reduces the number of single elements concerned in the production of the current. The manner in which this is achieved has already been described (see p. 72). The E.M.F. produced by dynamos can be reduced by inserting resistances in the shunt circuit that excites the magnets. The strength of the field is thus reduced and the E.M.F. diminished.

In spite of this arrangement the E.M.F. produced by dynamos is usually too high for many purposes, and the E.M.F. in the circuit is still further reduced by inserting resistances in it made from wire of high specific resistance, or by using only a fraction of the main current for the electrolysis. The alloys used for these resistances are the following : ‘German silver,’ ‘Rheotan,’ ‘Nickelin,’ ‘Manganin,’ and ‘Konstantan.’ Of these the alloys of manganese and copper, and of nickel, manganese, and copper, are the most satisfactory, as their resistance does not vary much with the temperature. These resistance

coils of wire are employed with all forms of current producer, they are extremely convenient in use, and they enable one to obtain the desired current strength within extremely narrow limits. In order to reduce the current from any source of electrical energy to the desired strength, one might stretch out a length of wire made from one of these poorly conducting alloys, and by means of a sliding contact take the current from any desired point

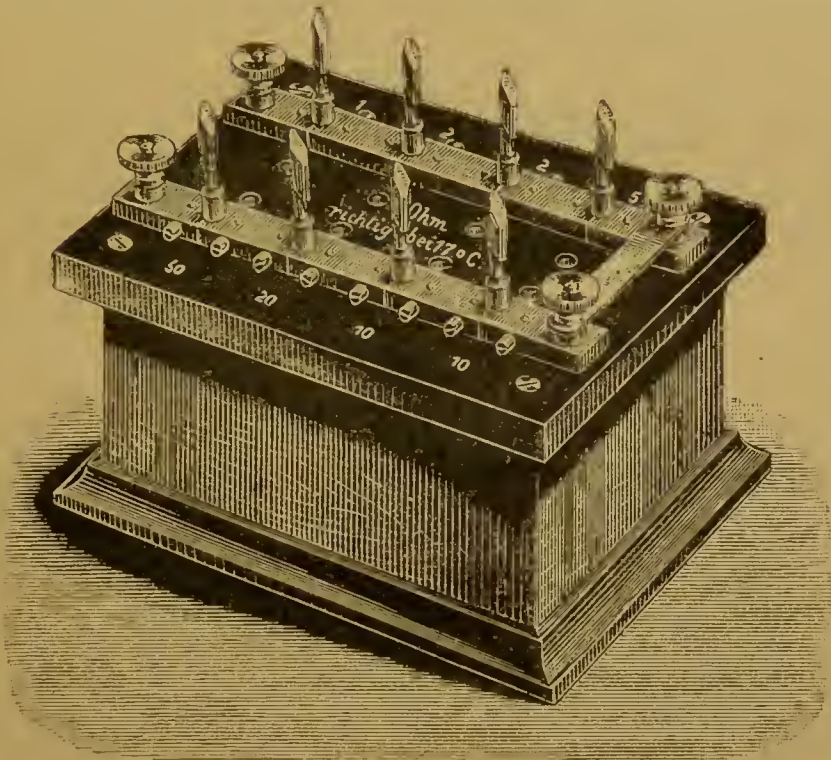


FIG. 22.—Resistance Box with Plug Contacts.

upon it. Such a simple arrangement is in most cases, however, not sufficient.

The customary form is shown in fig. 22. The insulated wire is wound into rolls or coils, the ends of these are soldered to brass connections arranged in order upon a wooden or slate base, and the well-insulated coils are enclosed in a box having this base as its cover. The brass pieces that represent the terminals of the coils are so

arranged that by the use of plugs they can be put in or out of circuit as desired. The resistance of the coils is expressed in ohms. They are arranged in the box in order of value, in a similar manner to that found in a set of weights, so that any resistance between 1 and 100 ohms can be produced. If all the plugs be inserted as shown in the illustration, the current passes entirely through the pieces of brass upon the cover of the box, and does not travel by any of the coils. Another form of resistance box

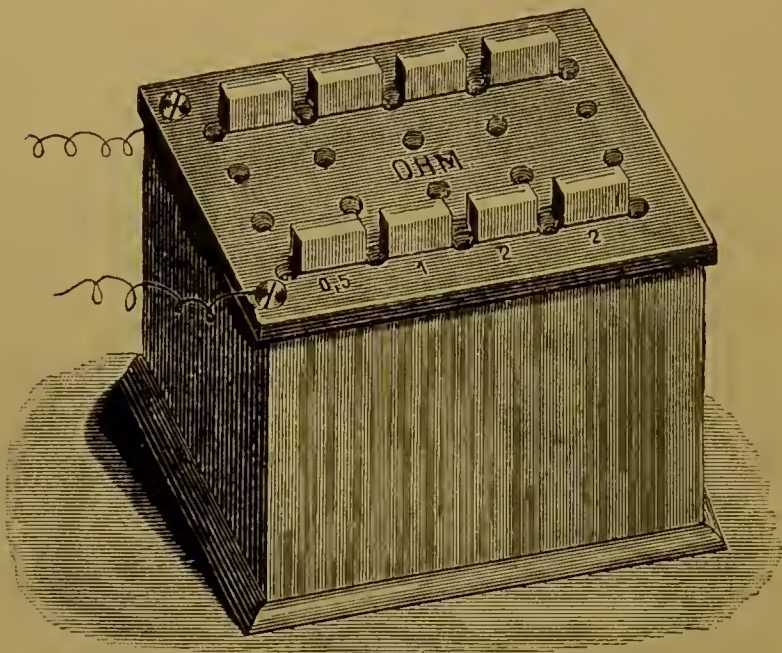


FIG. 23.—Resistance Box with Mercury Contacts.

is shown in fig. 23. In this case the ends of the coils are brought into small depressions, or cups, filled with mercury when the box is in use, and bent pieces of stout copper wire are used instead of plugs, to place the coils out of circuit.

One can make a similar variable resistance of less range by forming spirals of 'Manganin' or 'Nickelin' wire of different thicknesses, and by fixing these upon a frame, as shown in fig. 24. The ends of the wire

are soldered to stout copper wires which dip into mercury contact cups. If small binding screws be used with this resistance, the whole or part of any division of it may be cut out by binding two neighbouring wires together.

Since it is not necessary in the greater number of electrolytic separations to use resistances of any definite and fixed value, one frequently finds resistances in use which have not been standardised, and in which the contacts are made not by means of plugs or of mercury cups, but by means of the so-called 'sliding contacts.' Figs. 25 and 26

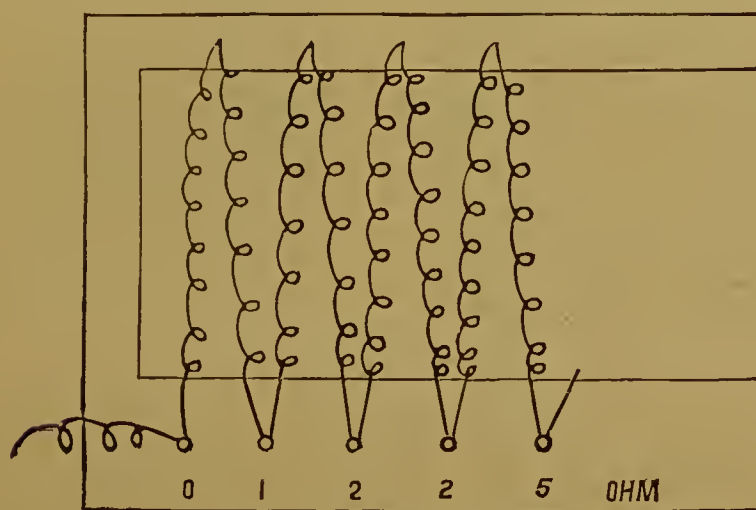


FIG. 24.—Frame Resistance.

are illustrations of this type of resistance ; many other forms of it exist.

The wire for the separate coils can be roughly measured according to the resistance data supplied by the manufacturer, and the arrangement of the coils upon the frame does not follow any order of value. When very strong currents are being employed it is preferable to use strips of thin sheets of the different alloys, in place of wire, in resistance frame.

If one desires to employ the second method for the production of feeble currents—that in which only portion of the main current is utilised—the following arrangement is

adopted. A strip of sheet brass, or a strip of one of the above-named alloys, is fastened in zigzag manner upon a small board, and the bends of the strip of brass or other alloy are soldered to brass pins or to the usual form of bind-

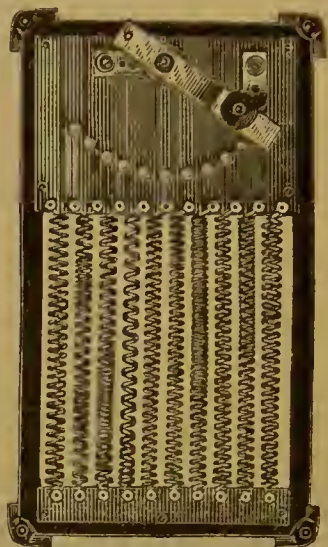
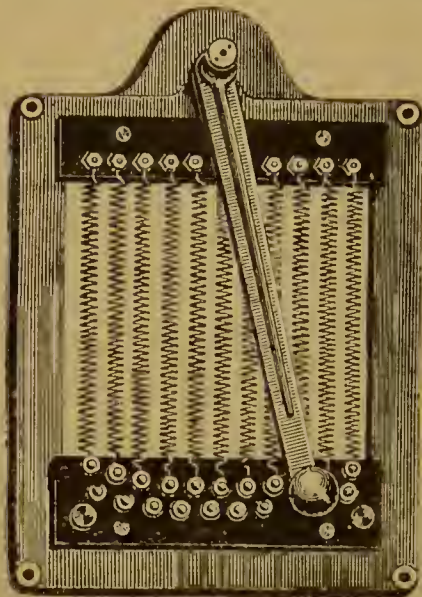


FIG. 25.—Adjustable Resistance. FIG. 26.—Adjustable Resistance.

ing screws, so that the current may be led from any of these points at will. This instrument is inserted in the main current circuit, and by use of these numerous contacts any desired fraction of the main current is switched off through a shunt circuit containing the electrolytic cell.

PART III

THE ELECTROLYTIC PROCEDURE

A. INTRODUCTORY

IN order that the current produced by any source of electrical energy may exert its dissociating influence upon a salt solution, it is necessary that suitable conductors should be chosen whereby the current may be led to and from the liquid. These conductors or 'electrodes' may be formed of different metals or of carbon, but for analytical work only those of platinum are employed. Platinised sheets of other metal have not proved serviceable ; and although gold has proved suitable in certain instances, yet platinum is to be preferred.

The electrode material must not only be proof against the acids used to dissolve the deposited metal, when the electrolysis has been completed and the deposit weighed, but must be also proof against the action of the anions liberated during the electrolysis.

For example, gold would be useless as an electrode material for the electrolysis of chloride or alkali-sulphide solutions. Even platinum is slowly attacked by chlorine, and on this account the electrolysis of solutions of chlorides is undertaken in as few cases as possible. If a solution of a zinc salt solution be electrolysed with a platinum kathode, a black deposit will remain upon the latter—especially noticeable at that part of the electrode which cut the level of the electrolyte—when the zinc has been dissolved off.

This deposit is insoluble in acids. According to Vortmann and others, it consists of finely divided platinum, and its removal from the electrode is difficult and is harmful to the latter.

In order to avoid this cause of injury to the platinum electrode, it is customary when zinc is to be deposited to coat the electrode previously with silver, copper, or tin. The surface of the electrodes is generally smooth, but it has been found that in certain cases it is more advantageous to use electrodes that have become roughened by frequent use, or that have been artificially made dull and dead by means of the sand-blast.

Peroxide deposits and also metallic deposits of antimony adhere better to such a roughened surface. The strength of the sheet metal used for the electrodes should not be too low ; the metal ought to be sufficiently thick to resist any mechanical strains to which it may be subjected. Electrodes made from an alloy of platinum and iridium are found to resist both the chemical action and mechanical wear and tear of use, better than those made of platinum alone.

As regards the form of the electrodes, great differences may exist, and practically all the possible forms are in actual use. They may be divided into two broad classes. Under the one come all those electrodes used in pairs for the electrolysis of liquids contained in beakers or other non-conducting vessels. Under the other are grouped those forms in which one electrode acts as a basin or vessel for holding the electrolyte.

Neither class possesses decisive advantages in all cases ; but each is found to be especially convenient in particular separations.

The 'basin electrode' is used in two forms. That recommended by Classen is shown in fig. 27, and has no lip.

The form shown in fig. 28 is recommended by N. v. Klobukow. It possesses a spherical cup-shaped bottom, per-

pendicular sides, and a lip. The latter form may be slightly more convenient for use when it is necessary to calculate the electrode surface covered by a definite volume of the liquid, but apart from this it has no advantage over the former. It is of great convenience to have marks upon the inner surface of the walls of the basin which denote the superficial area covered by the liquid when standing at any particular height in the basin ; since this simplifies the work when carrying out electrolytic depositions by means of definite current densities.

The basin shown in fig. 27 is about 9 cm. in diameter and about 4 cm. in depth ; its capacity is between 200 and 250 c.cms. liquid.



FIG. 27.—Basin for Electrolysis.



FIG. 28.—Basin for Electrolysis.

The other electrode for use with this basin can have many forms. The form shown in fig. 29 corresponds best to the shape of the basin, and secures a uniform current density ; it suffers from the disadvantage that, in spite of the openings in its sides, the volume of liquid enclosed within it passes but slightly into circulation. The 'saucer electrode,' shown in fig. 30, possesses a round hole at its deepest part ; while the 'disc electrode,' shown in fig. 31, is pierced with many round openings. These two forms are more satisfactory than the first, since they hinder the circulation less, and the holes permit the escape of the gases liberated at their surface.

The separate parts of these electrodes should be riveted together ; if they should be soldered even with gold, the

solder will be speedily dissolved away when they are used as anodes.



FIG. 29.
Basin Electrode.



FIG. 30.
Saucer Electrode.

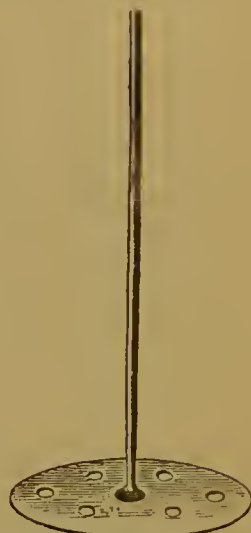


FIG. 31.
Disc Electrode.

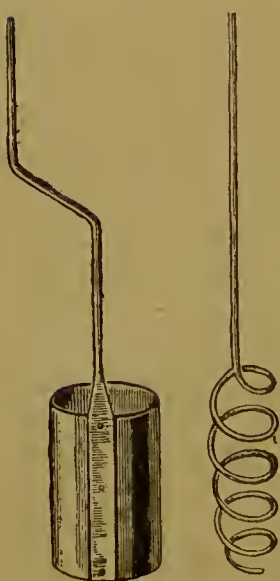


FIG. 32.—The Mans-
field Electrodes.

Turning to the other group of electrodes, many forms are found to have been proposed and used. The simplest arrangement is that of two sheets of platinum opposed to one another in the vessel containing the electrolyte ; but this is seldom adopted. In some cases a fork-shaped anode is used with a single sheet of metal as kathode, in order to obtain a uniform coating upon each side of the latter. The forms most in use, however, are a cylindrical or conical sheet electrode, enclosing a similarly shaped spiral of thick platinum wire. One of the oldest types of this arrangement is the so-called Mansfield electrode, shown in fig. 32. This consists of a closed platinum cylinder, and of a platinum wire spiral used within the

cylinder. The first practical attempts to effect electrolytic determinations of metals were made with this form of electrode.

If one decides to make use of this form, it will be advisable to cut the cylinder through in the direction of its axis, and also to bore some holes at other points in it, in order to facilitate the circulation of the electrolyte, and also to allow the deposition to occur to some extent upon the outer side of the cylinder. The conical jacket electrode shown in fig. 33 is also a form much used, and

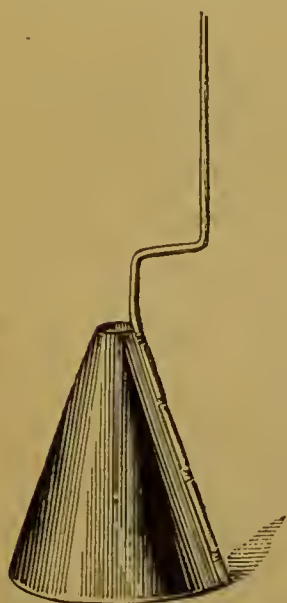


FIG. 33.



FIG. 34.



FIG. 35.

FIGS. 33-35.—Cone-shaped and Spiral Electrodes.

in this case the electrode is better when provided with openings to promote the circulation of the electrolyte. Figs. 34 and 35 show the forms of spiral used with this jacket sheet electrode. The form shown in fig. 36 is, however, to be preferred if a uniform current density at all parts of the surface of the cone is required. The cone is generally used about 8 cm. in height, and about 6 cm. in diameter at its base. If these jacket electrodes be provided with an opening parallel to their axis, they possess

the advantage that when the electrolysis is completed they can be lifted directly out of the solution. The gas bubbles that are given off from the lower parts of the wire electrode also aid the thorough mixing of the electrolyte during the electrolysis. The disadvantage of these forms lies in the difficulty of obtaining a uniform current density at all parts of the sheet electrode, and on this account these electrodes cannot be used in performing some of the more particular electrolytic depositions.

As holder for the electrodes, a stand having a heavy cast-iron base into which a strong glass rod is fixed will be found to answer best. Upon this glass rod slides an arm of brass, copper, or aluminium, capable of being fixed at various heights, and bearing two binding screws, one for connection with the current supply, the other for connection with the electrode. If the jacket electrode is to be employed, either two such stands are used, or a compound holder such as that illustrated in fig. 36 is used, in which the conducting parts *a* and *b* are separated by an insulating piece *x*.

If the basin electrode be used, one of the arms must be bent into a ring, and this is provided on its upper side with three platinum points, which make the electrical contact between the ring and the basin. When the column of the stand is of glass, both arms may be fixed upon it, as shown in fig. 37.

Another form suitable for use with the basin electrode consists of a turned wooden foot having a thick metal wire bent into a circle fixed upon it. The basin rests firmly upon this, while a bent metal arm, fixed at one side of this wooden base, serves to hold the disc electrode over the middle point of the basin. This form of holder has not come much into use, one of its disadvantages being that it is impossible to heat the electrolyte during the electrolysis by means of a small burner placed beneath the basin.

In order to avoid loss of the liquid during the electrolysis, the basin or beaker must be covered with a large clock-

glass. When the former is used to hold the electrolyte, this glass will answer if it have only a hole through its centre ; but when a beaker is used, it is necessary to have a narrow slot in the glass cover, extending from the circumference to the centre.

It is especially necessary in electrolytic work to see that the electrodes are perfectly clean ; with dirty electrodes it is impossible to obtain a uniform and adherent deposit. Films of grease, which can be produced merely by passing

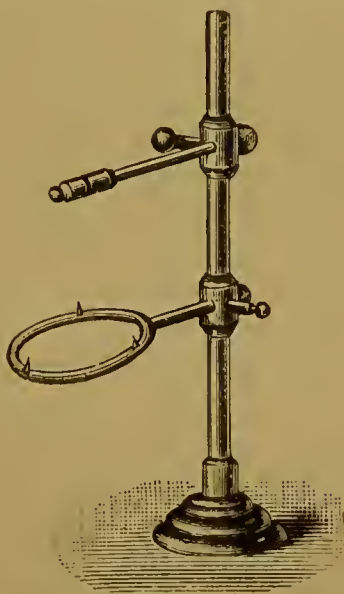
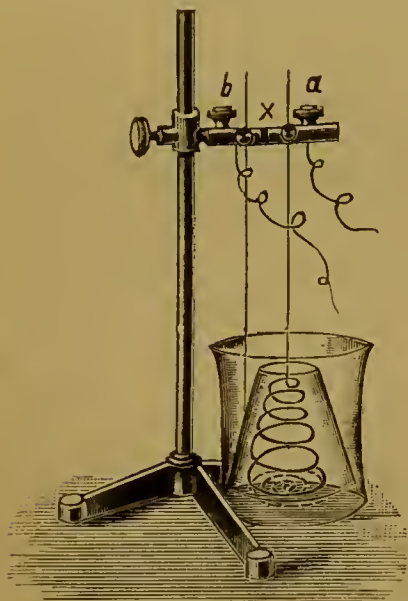


FIG. 36.—Stand for Electrolysis. FIG. 37.—Stand for Electrolysis.

the fingers over the electrode surface, are especially detrimental.

If an electrode that has been soiled in this way cannot be freed from its impurity by heating to redness, or by treatment with acids, it will be necessary to heat it with fused acid potassium sulphate or with borax, or to clean it by mechanical means with fine sea-sand. The methods first named are least harmful to the electrode, and are to be preferred, when effective. The electrode when perfectly clean is well washed, and is dried by heating.

In order to carry out the electrolysis, the prepared

solution of the metallic salt containing the necessary additions of other chemicals is placed in the platinum basin, or in the beaker designed for use with one of the sheet electrodes. For electrolytic analyses, the volume of liquid should lie between 150 c.cms. and 200 c.cms. ; the volume of liquid to be dealt with must therefore be brought within these limits by concentration or dilution, as the necessities of the case demand. If the jacket electrode, either in cylinder or cone form, is being used, the distance apart of the two electrodes will be alike at every point if care has been taken to centre the inner electrode properly when fixing it in the holder. Care must also be given to guard against any displacement or contact of the two electrodes when placing them in, or when taking them out of, the liquid in the beaker. When the basin electrode is used, attention must be paid not only to the central position of the disc electrode, but also to its height above the bottom of the basin. This should lie between 1.5 and 2.0 cms. in all cases. The clock-glass used for covering the vessel in which the electrolysis is performed must be laid on at the commencement. When a metallic deposit is to be obtained, the basin or the sheet electrode is used as kathode ; but when a deposit of the metal as peroxide is desired, the current direction is reversed, and the basin or sheet electrode is used as anode.

The current density given in the directions for the different depositions in the following pages is always calculated upon the superficial areas of these electrodes, and not upon those of the wire ones. When the current connections are first made for such an electrolytic cell as that described above, a very large resistance is always used in the circuit ; and the ampères having been calculated that will yield the desired current density with the electrode surface that is immersed, the resistance is reduced until this current strength is obtained. Since the interior surface area of the form of platinum basin customarily used (see fig. 27), having a diameter of about 90 mm. and a

depth of about 40 mm., is only determined with difficulty mathematically, one uses the following data for the current density calculation : 125 c.cms. liquid cover 100 sq. centimetres, and 180 c.cms. cover 150 sq. centimetres of the interior surface of the basin.

These ratios are sufficiently exact for use in most cases, since the maintenance of the current density within more accurate limits is unnecessary.

The concentration of the electrolyte undergoes change during the electrolysis, and in most instances this occasions an increase in the resistance it offers to the passage of the current. If the external conditions remain the same—i.e. if the E.M.F. of the battery or dynamo, and resistance of the external circuit, remain unaltered—the current strength, and therefore the current density at the electrodes of the electrolytic cell, will be diminished. In order to maintain the current density at the kathode (when peroxide depositions are in progress—at the anode) at a definite value, many measurements must be made during the course of the electrolysis, and the strength of the current must be increased proportionately to the growth of the resistance of the electrolytic cell, by diminishing the resistance that has been inserted in the external circuit. The E.M.F. measured at the terminals of the electrolytic cell is always a guide to the resistance of the cell, and by frequent measurements one can observe the increase in this as the electrolysis proceeds. As already mentioned, it is now customary to calculate the current density—that is, the strength of the current in ampères per unit of surface—upon a superficial area of 100 sq. centimetres.

This 'normal density,' as it is called, is used both for the kathode, and for the anode when peroxide deposits are being obtained. For electrodes of other size the calculation is simple. In the following special part of this work all the current strengths given are calculated for a superficial area of 100 sq. centimetres, even when this is not particularly noted.

As regards temperature, in most cases the electrolysis can be conveniently carried out at the normal indoor temperature of 20°C . (68°F .) The electrolyte frequently increases in temperature when strong currents are employed, but it is often advisable to heat the liquid by the aid of some external source of heat, in order to reduce the resistance it offers to the current, and to lessen the time necessary for the complete deposition of the metal. A high temperature is also often requisite in order to obtain a metallic deposit possessing the desired physical characteristics. If then it be desired to electrolyse a warm or hot solution, a burner with a small easily regulated flame is placed under the basin or beaker containing the liquid. One may use for this purpose either an ordinary Bunsen burner from which the vertical tube has been removed by unscrewing, or one may make use of a small Bunsen burner especially designed for this purpose, possessing a horizontal mixing tube turned upwards at its end. In order to obtain an equal and regular temperature, a piece of asbestos paper or board is loosely placed under the basin or other vessel, so that the latter is heated by the intervening air rather than by direct contact with the hot asbestos. In the majority of instances it is sufficient to lead strong currents—1.0 to 1.5 ampères—through the warmed electrolyte; the temperature then remains about the same. When this is not feasible the temperature of the electrolyte will fall from 60°C . to about 40°C . during the electrolysis, if no external heating be used. Such a fall in temperature ought not to prove detrimental to the results obtained with any really trustworthy method, and therefore, in the conduct of technical electrolytic analyses, the use of a burner for maintaining the temperature has been discontinued.

The completion of the deposition and end of the electrolysis can be determined in many ways. When the deposit is a coloured one—as, for example, that of copper or of the peroxides—the observation is carried out by adding a little

distilled water to the electrolyte, and thus covering a fresh portion of the kathode surface with the liquid. This newly covered surface is examined after an interval of five or ten minutes ; if no trace of a deposit be visible, the electrolysis is completed. When the basin electrode has been used, instead of adding water to the electrolyte, a small strip of clean platinum foil is hung over the edge of the basin, so that it dips into the liquid.

When the jacket electrode is used, it is extremely easy to change the first electrode for a second one free from any deposit. These methods are, however, not applicable in the case of those metals the deposits of which differ little from that of the platinum in colour—as, for example, the deposits of cobalt, nickel, iron, and silver. In these cases the test is usually made by withdrawing a small portion of the electrolyte by means of a small pipette, and by applying to this small test portion some delicate chemical test. If no reaction for the concerned metal is obtained, one concludes that the last traces have already been removed from the electrolyte by the action of the current.

When the electrolysis is completed, the circuit is broken, the electrodes are freed from the binding screws, and the liquid is poured out of the basin, or the jacket electrode is lifted out of the liquid in the beaker. The portion of the liquid that clings to the deposit is washed away with distilled water, and the water is then itself removed by rinsing the deposit with strong alcohol. The final drying is accomplished either over the open flame, upon a heated asbestos or iron plate, in the air-bath at 100°C. , or in a desiccator, according to the nature and character of the deposit. The alcohol is used to prevent, as far as possible, the oxidation of the moist metallic coating.

In many electrolytic depositions the breaking of the circuit leads to a re-solution of the deposited metal by the electrolyte, and in these cases it is necessary to displace and wash out the electrolyte before breaking the circuit. This is accomplished by hanging over the side of the vessel

a small siphon filled with water, and by adding distilled water to the vessel as the original liquid is carried away by this siphon. A conducting medium thus remains between the two electrodes, the current continues to pass in the original direction, and only after suitable dilution of the original electrolyte is the circuit broken, and the electrode with its deposit removed for further treatment in the usual way. When the jacket electrode has been employed, one may avoid using this displacement method of removal of the electrolyte by a quick withdrawal of the electrode from the electrolyte. The former method ought to be used for deposits of copper from nitric acid solutions, of antimony from sodium sulphide solutions, of lead peroxide from nitric acid solutions, and of other metals ; but one may even in these cases substitute for it a rapid emptying of the basin without introducing any serious error into the results. The weight of metal which can pass into solution again during the few seconds required for pouring off the electrolyte and diluting the remainder, varies with the metal, the solution, and the duration of the operation ; but experiments have shown that it is, as a rule, between $\cdot 0004$ and $\cdot 001$ gram. The electrode bearing the dry deposit must never be weighed until it has cooled down to the temperature of the balance room.

Since a repetition of any experiment is only possible when data concerning the concentration and temperature of the electrolyte, the strength and electro-motive force of the current, and the superficial area of the electrodes have been kept, it is advisable even from the commencement of the experiments to record all these details, as well as the observations made during the progress of the experiment, and the results obtained, in some such form as the following :

Experiment.—(Example—Copper, or separation of copper and lead.)

Electrolyte.—(1 gram. CuSO_4 ; 5 c.cms. HNO_3 ; 150 c.cms. H_2O .)

Source of Energy.—(Two accumulator cells in series.)

Electrodes.—(Basin—jacket electrode—or foil.)

OBSERVATIONS AND MEASUREMENTS

Electrode area in sq. centimetres	Electrodes; distance apart	Volume of the electrolyte	Temperature of the electrolyte	Time of current measurement	Current strength in amperes	E.M.F. at the electrodes in volts	Resistance of the cell in ohms ¹

Results

Current density (per 100 sq. cms.)	Character of the deposit
E.M.F.	Used for analysis gram.
Temperature	Found gram.
Duration	Difference gram.
	Remarks

B. DEPOSITION OF THE METALS FROM SOLUTIONS OF PURE SALTS

In the following division of this work a number of different methods are given under the headings of the individual metals, by which the separation of the concerned metal can be effected.

These will be found to include not only electrolytic methods of a particular class, but also practically all the methods in actual use, whoever may have been their authors.

Those methods, which are easily carried out, and which, in some cases by variation in the conditions, can be made to yield reliable results, have received especial attention; since such methods have been adopted in some technical laboratories as substitutes for the older analytical processes.

In all cases the necessary information concerning

$$^1 \text{ Resistance} = \frac{\text{E.M.F.}}{\text{current}}$$

current density, concentration, temperature, and voltage has been given. A very full list of references to original papers will facilitate the consultation of these when necessary, and will enable the reader to obtain a comprehensive survey of the methods proposed up to the present date. It will also serve to check the very common rediscovery of old methods by new workers in this branch of science.

Those separations which are of technical importance have been indicated, so that the choice of methods for practice by the novice has been simplified as far as possible.

COPPER

Copper was the first metal of which proof was given that it could be deposited quantitatively by electrolysis. Electrolysis was thus shown to be applicable to analytical purposes.

Copper is distinguished from other metals by the ease with which it can be deposited from acid solutions, and by the character of the deposit so obtained. This is nearly always bright red in colour, and of a metallic lustre. The position of copper below hydrogen in the series of metals given in Chapter VII (p. 35) signifies that the metal can be deposited without difficulty, especially from solutions containing free acid. In such solutions the decomposition value of the salt of copper is comparatively low, and the deposition can be effected with a very small expenditure of energy.

An E.M.F. of 1.8 volts suffices to separate copper from solutions containing nitric acid ; from solutions containing ammonia a voltage rather lower than this is sufficient ; while from solutions containing ammonium oxalate only 1.5 to 1.6 volt is required.

Solutions of copper sulphate or copper nitrate containing free nitric acid are especially suited for laboratory electrolysis ;¹ but the amount of free acid present must not be

¹ *Zeitschr. f. anal. Chem.*, 19, 1.

allowed to exceed 8 to 10 per cent.¹ For the carrying out of such an electrolysis a weighed amount of copper sulphate, generally about 1 grm., is dissolved in water, the solution is diluted to about 150 c.cms., and from 3 to 5 per cent. by volume of conc. nitric acid (sp. gr. 1.40) is added to it. The solution is heated to 50° or 60° C. in the basin or in the beaker in which the electrolysis is to be performed, and a current of about 1 ampère is passed through it. The E.M.F. should be from 2 to $2\frac{1}{2}$ volts.

The reddish deposit of metallic copper upon the kathode can be noticed immediately the circuit is completed. The current is allowed to continue until the blue copper solution appears to have lost all its colour; this result should be obtained in the course of about two hours. Before the circuit is broken, however, it is necessary to prove that the whole of the copper has been deposited. The complete separation of the copper contained in 1 grm. of copper sulphate, which contains theoretically 25.33 per cent. Cu, should require, with the strength of current named above, from two to three hours. In order to test whether in a particular case traces of copper are still present in the solution, sufficient water is added to the electrolyte to cause the immersion of a clean portion of the kathode. As the reddish colour of the deposited copper is very distinct against the platinum kathode, a ready means of checking the completion of the deposition is afforded.

After the addition of water to the electrolyte, the current is allowed to continue for ten or fifteen minutes, and the freshly immersed surface of the kathode is then examined for a thin coating of copper. A more delicate method of determining when the electrolysis is complete consists in the withdrawal of a very small quantity of the electrolyte by means of a glass tube which has been drawn out at one end to a fine jet, and in the testing of this by chemical methods. The two reactions made use of for this purpose are those

¹ *Berg- u. Hütten-Zeit.* 21, 220.

with sulphuretted hydrogen and potassium ferrocyanide ; the test with ammonia is not sufficiently sensitive for such small amounts of copper. The liquid that has been withdrawn is treated with a few drops of sodium sulphide solution, after addition of acid if it be a neutral or alkaline solution of copper ; the presence of traces of copper is indicated by a distinct brown colour of the solution. The use of sulphuretted hydrogen gas is less convenient. In order to apply the potassium ferrocyanide test, a few drops of the solution of this salt are placed in each of two test tubes, the liquid in each is acidified with a little hydrochloric acid, and the solution withdrawn from the electrolyte is added to the contents of one of these test tubes. On viewing the tubes against a white background, the presence of a very small amount of the reddish ferrocyanide of copper is easily detected. One can also mix finely ground potassium ferrocyanide with a drop or two of hydrochloric acid upon a porcelain tile, and allow the solution which is to be tested to fall in drops into the middle of the mixture ; a reddish coloration will appear at the edges of the mixed solutions if traces of copper be present.

When it has been proved that the whole of the copper has been removed from the solution, it is simply necessary, if a jacket electrode has been used, to remove this from the holder, to lift it quickly out of the solution, and to wash it under a running stream of water in order to free it from the adherent acid liquid. When a basin has been used as negative electrode, this would demand some little time, and it is necessary to proceed differently if all danger of the acid liquid acting upon the deposit of copper is to be avoided. In this case the copper must be washed before the current is discontinued. This is effected by using a siphon to remove the electrolyte from the basin, while water is allowed to flow in. In this way the acid in the solution becomes diluted to a point at which action upon the deposit is impossible. The contents of the basin are then emptied out, it is rinsed a few times with water, and

lastly with strong alcohol, and quickly dried in an air bath or by the naked flame.

The solvent action of the remaining electrolyte upon the deposited metal is, it must be admitted, not very great, since a portion of the nitric acid present at the commencement of the electrolysis will have been converted into ammonia. Experiments made with a copper sulphate solution to which 8 per cent. of nitric acid had been added, which was electrolysed for an hour with a current of 1 ampère, showed that 0.004 gram. of the deposited copper was dissolved in each case by the remaining solution in a quarter of a minute from a surface of 100 sq. centimetres. An expert analyst would never require such an interval of time for disconnecting and emptying the basin; and, further, the loss of 0.004 gram. would be unimportant in its effects upon the results of technical analyses.

The proposal of Rüdorff to add sodium acetate to the electrolyte, instead of breaking the circuit in order to carry out the washing, is likewise a useful one.

The deposit of copper obtained from a solution containing free nitric acid possesses a bright red colour, and is of crystalline structure. If the current be passed for a considerable time through such a solution, a portion of the nitric acid will be itself decomposed with formation of ammonia; this ammonia neutralises a further portion of the free acid, so that the amount of free acid present diminishes as the electrolysis proceeds.

The separation of copper from its solution containing free nitric acid can also be effected by allowing a weak current to act for a longer period of time. Thus, the solution of which details have been given above may be left overnight with a current of from 0.2 to 0.3 ampère passing through it; the deposition will be complete by the next morning, and no heating of the solution prior to the commencement of the electrolysis will have been necessary.

In this case it is, however, requisite to increase the amount of free nitric acid added to the solution; an

addition of 10 c.cms. for a volume of 150 c.cms. of the solution suffices. In the presence of insufficient free acid, and of increase of the ammonia contents of the solution, the copper is deposited in a brown spongy form, which adheres so slightly to the electrode that, even on washing, portions become loosened and are lost. Such bad-coloured spongy deposits are not adapted for weighing, and the results obtained with them are inaccurate.

The fact that it is possible to obtain satisfactory deposits of copper from the solutions containing free nitric acid, with current densities up to and over 3 ampères, is worthy of notice.

In the same manner that copper may be separated from solutions of its sulphate after addition of nitric acid, it is possible to obtain useful deposits from solutions containing free sulphuric acid.¹ The amount of acid present must, however, not exceed 8 to 10 per cent.

In order to carry out this method, 1 grm. of copper sulphate is dissolved in about 150 c.cms. of water, 2 to 3 c.cms. of conc. sulphuric acid (or a corresponding amount of dilute acid) are added, and the solution is then electrolysed at the normal temperature with a current density of 1 ampère. In the course of one and a half or two hours the whole of the copper will be separated as a red deposit. When the amount of copper is considerable, this deposit is never so brilliant in colour as the deposit obtained from nitric acid solutions, but it nevertheless yields exact results.

The E.M.F. required for the electrolysis of sulphuric acid solutions is from 2.5 to 3 volts.

It is possible by warming the solution to lessen the time required for this electrolysis. This diminishes the resistance of the electrolyte, and if the current conditions remain unaltered in the external circuit, the current will consequently increase, and with it the amount of deposit, in a definite time. When using solutions con-

¹ Luckow, *Dingl. polyt. Jour.* 1865, 177; Gibbs, *Zeitschr. f. anal. Chem.* 3, 334.

taining free sulphuric acid in the proportion described above, it is not wise to allow the current density to exceed 1·5 ampères per 100 sq. centimetres, because with higher current densities, in spite of the free acid present, the deposit has a tendency to separate in a less compact and somewhat spongy form. In order to gauge the end of the electrolysis, the same reactions are made use of as with nitric acid solutions.

The same precautions with regard to stopping the current and washing the deposit must also be observed. The deposition of copper from a sulphuric acid solution was the first example of the use of electrolysis for technical analysis.

Gibbs, in the year 1864, determined the copper in copper-nickel coinage by this method, and in 1865 Luckow made use of this same process for the determination of copper in the metal used for the fireboxes of locomotives.

One would expect that copper could also be obtained as a beautiful deposit from the neutral sulphate solution, since in this case the electrolyte gradually becomes acid owing to the formation of sulphuric acid at the anode. This assumption is found to be correct; but the resistance of the neutral electrolyte is so great that an E.M.F. of 6 volts is requisite at the commencement in order to obtain a current strength of ·5 ampère. Heating this electrolyte does not much increase its conductivity.

For practical work, it is therefore better to lessen the resistance by the addition of a few cubic centimetres of nitric or sulphuric acid.

Luckow and Drossbach have made attempts to electrolyse copper sulphate solutions to which excess of ammonia had been added; but bright deposits could only be obtained when very feeble currents were employed. Oettel¹ and MacCay² found, however, that the conditions were much

¹ *Chem. Zeitg.* 1894, 879; *Zeitschr. f. Elektrochem.* 1894, 142.

² *Chem. Zeitg.* 1890, 509.

improved by the addition of definite amounts of ammonium nitrate to the solution.

In order to carry out this electrolysis 1 gram. of copper sulphate and 4 grms. of ammonium nitrate should be dissolved in water, and ammonium hydrate should be added until it is present in slight excess. The deep blue solution is diluted until it occupies about 150 c.cms., and it is then electrolysed at the normal temperature with a current of from .1 to .3 ampère. The E.M.F. at the commencement of the electrolysis is about 2 volts; during its course, however, it rises to about 3 volts. At the end of a period of from six to seven hours the deposition is complete, the copper being obtained as a brilliant metallic coat. If the amount of ammonium nitrate be decreased, or if that of ammonium hydrate be increased, there is some danger of the copper separating in the brown and spongy form. This method can be employed for effecting copper separations during the night.

While copper can be separated in bright metallic form from solutions of the sulphate and nitrate containing free sulphuric or nitric acids, experiments with cupric chloride and hydrochloric acid have shown that the solution of this salt is not suited for analytical purposes, since the copper has a tendency to separate from it in the spongy form.

It may be noted here that it is necessary to avoid as far as possible the use of chlorides for electrolytic work if metal electrodes are to be employed, as the free chlorine produced by the electrolysis has always some action upon them.

Rüdorff¹ has nevertheless found that a useful deposit can be obtained from solutions of the chloride to which ammonium nitrate and excess of ammonium hydrate have been added. To obtain a deposit from such a solution, .5 to 1.0 gram. of cupric chloride and 4 to 5 grms. of ammonium nitrate are dissolved in 100 to 125 c.cms. of water, and 25 to 30 c.cms. of ammonium hydrate are added. This solution is then electrolysed at the normal temperature with a

¹ *Berichte*, 21, 3050.

current density of about 1 ampère ; the E.M.F. required is from 3.3 to 3.6 volts.

To effect the separation of the copper contained in 1 gm. of cupric chloride, from two and a half to three hours are necessary. During the electrolysis the temperature of the solution is found to increase slightly, and it is therefore better to carry out the deposition at a temperature of 50° C. by means of a feebler current. The deposit, which is at first a brilliant red, becomes later dull. In spite of this change in its character, it is, however, not spongy, and it is well suited to analytical requirements.

The employment of copper salt solutions to which an excess of potassium cyanide had been added dates back very many years, since in 1840 Ruolz had suggested the use of this form of solution for electrotyping purposes. Later it was suggested by Luckow¹ and Moore² for analytical work.

The solution is prepared by dissolving 1 gm. of copper sulphate in a small amount of water, and by adding sufficient potassium cyanide solution³ to this, to cause the re-solution of the precipitate of cupric cyanide which is at first formed.

The solution is then made up to 125 to 150 c.cms. by the addition of water. The double cyanide of potassium and copper which is present in this solution requires at least 2.2 volts for its decomposition. If a current of 1 ampère be passed through it at the normal temperature, an E.M.F. of from 5.2 to 5.8 volts will be found at the terminals ; if, however, the electrolyte be heated to 60° C., the same current density at the cathode can be attained with an E.M.F. of 4.2 volts. The copper contained in 1 gm. of copper sulphate will be completely deposited in an hour and a half under these conditions. The deposit obtained from

¹ *Zeitschr. f. anal. Chem.* **19**, 1.

² *Chem. News*, 1886, **53**, 209.

³ The purer the potassium cyanide the better the results. The commercial article is too impure to be used for this purpose.

cyanide solutions of copper does not possess the crystalline structure characteristic of the deposits obtained from nitric acid solutions, but is a pale rose-coloured homogeneous coating.

The whole of the copper will be deposited from a solution heated to 60° C. in two hours, if a current of $\frac{1}{2}$ ampère should be used in place of the 1 ampère named above.

This method of deposition from cyanide solutions is also adapted for use with still feebler currents ; and it is also useful when circumstances prevent close and constant attention to the course of the electrolysis.

The use of the double oxalate salt of copper and ammonia for electrolytic separations of the copper has been discussed by Classen and von Reiss¹ and by Classen and Bongartz.² It has been found that better results are obtained by use of this salt in solutions made acid with oxalic acid than in the originally used neutral solutions.

In order to carry out this electrolysis, 1 grm. of copper sulphate and 4 grms. of ammonium oxalate are dissolved separately in water. On mixing these two solutions, the precipitate which first forms is seen to redissolve. The solution is heated to between 50° and 60° C., and a current of $\frac{1}{2}$ to 1 ampère intensity is passed through it, after first adding some few cubic centimetres of a saturated solution of oxalic acid, sufficient to cause the electrolyte to give a distinctly acid reaction with litmus paper. In the absence of this addition of oxalic acid, the deposit obtained quickly changes to a brown and spongy form ; whilst if too great an excess of oxalic acid be used, an insoluble form of copper oxalate separates at the kathode. It is on this account advisable to add the oxalic acid in small amounts only, from time to time, during the electrolysis. The oxalic acid is decomposed by the current with formation of carbon dioxide. A current of 1 ampère will deposit the copper contained in 1 grm. of copper sulphate from this electrolyte at a temperature of 50° to 60° C. in two hours, the E.M.F. necessary being from

¹ *Berichte*, 14, 1627.

² *Ibid.* 21, 2898.

2·8 to 3·2 volts ; while with a current of half this intensity the deposition would occupy two and a half hours, and the E.M.F. required would fall to between 2·5 and 2·8 volts. This method gives bright metallic deposits (the contrary assertions on this point are incorrect) when exact attention is paid to the necessary precautions, especially to those concerning the addition of the acid ; that is to say, continuous and close attention is required in order to obtain good results by its use. Since, however, there are other methods which are simpler and more conveniently carried out, which always yield reliable results, this method with double oxalates cannot be recommended.

Smith¹ has proposed the use of solutions containing phosphate of soda and free phosphoric acid.

Heydenreich² has, however, pointed out that the deposition from such solutions occupies a very long time (seventeen hours), and that the deposits are not bright. The E.M.F. required is from 2·4 to 3·0 volts. Brand³ has examined into the effects produced by the use of the alkaline pyrophosphates. The deposits obtained are fawn-coloured and dull, and the time required is excessive.

Other solutions that have been recommended are those containing sodium acetate with free acetic acid,⁴ and the tartrates of the alkali metals and of ammonium.⁵

The latter methods offer no advantages over those first described. The methods which are actually employed in technical laboratories as substitutes for the ordinary gravimetric or volumetric processes of analysis are exclusively those in which free nitric or sulphuric acid is used. When separations of metals have to be effected, the methods with potassium cyanide and excess of ammonia are also used.

¹ *Amer. Chem. Jour.* **12**, 329.

² *Berichte*, **1896**, 1585 ; *Zeitschr. f. Elektrochem.* **1896**, 151.

³ *Zeitschr. f. anal. Chem.* **28**, 581.

⁴ Warwick, in *Zeitschr. f. anorg. Chem.* **1**, 285.

⁵ Smith and others, in *Jour. Anal. and Appl. Chem.* **5**, 488 ; **7**, 189, 252.

With regard to the accuracy of the electrolytic methods for copper determination, it is proved that these yield results equal to those of the best purely chemical processes of analysis. Long practical experience is not required in order to obtain accuracy with these electrolytic methods.

It is customary to obtain the weight of the deposits to the fourth decimal place, and a difference of .001 grm. between successive determinations may be regarded as the maximum of the deviation that ought to occur.

IRON

Iron, in contrast to copper and the noble metals, belongs to that group of metals which cannot be separated from moderately acid solutions by the current or E.M.F. which it is customary to have at one's disposal for analytical purposes.

Since iron is precipitated from its solutions as hydroxide by ammonia and the alkaline hydrates, the use of these reagents for preparing the iron solution for electrolysis is also excluded. The choice is therefore restricted to the neutral salts, the double salts, and some complex substances. It has, however, been proved that complete deposition is not possible when neutral salts are electrolysed, and these are therefore unsuited for analytical purposes.

One of the best methods for the electrolytic separation of iron is that suggested by Parrodi and Mascazzini¹ and by Classen and von Reiss.² This depends upon the decomposition of the double oxalate of iron and ammonium.

In order to carry out this method, 1 grm. of ferrous sulphate or of ferrous ammonium sulphate is dissolved in a small quantity of water, and at the same time 5 to 6 grms. of ammonium oxalate are dissolved in about 100 c.cms. of water with the aid of gentle heat. The two solutions are mixed

¹ *Gazz. Chem. Ital.* 1879, B. 8.

² *Berichte*, 1881, 14, 1622, 2771.

by pouring the iron salt solution into the other, and the mixture is stirred until the first-formed precipitate has redissolved. If one proceeds in the reverse manner a ferrous oxalate will be precipitated, the re-solution of which is difficult.

The clear solution, which should measure about 150 c.cms., is now electrolysed with a current density of from 1.0 to 1.5 ampères, and with an E.M.F. of from 3.5 to 4.5 volts. The electrolysis can either be performed at the normal temperature or at 50° C. ; in the latter case the rate of deposition is increased. The length of time necessary to effect the deposition of the iron contained in the amount of salt named above will be about four hours with a 1-ampère current, and between two and a half and three hours with a current of from $1\frac{1}{2}$ up to 2 ampères.

It is also possible to carry out this electrolysis by means of a weak current of from .3 to .5 ampère strength, and in this case the separation can be effected during the night. It is necessary, however, when the lower current strength is adopted, to increase the amount of ammonium oxalate in the solution ; and it is also necessary to increase the current to a strength of at least 1 ampère at the end of the electrolysis, in order to effect the removal of the last traces of iron from the electrolyte. The ammonium oxalate is decomposed by the current, carbon dioxide is liberated at the anode, ammonium carbonate is formed in the solution, and the electrolyte becomes alkaline with separation of flakes of ferric hydrate. By use of a large amount of the ammonium oxalate salt, one can to a very large extent avoid this result.

If, however, in spite of this increase, ferric hydrate should be formed, it is possible to bring it into solution again by the addition of a small amount of oxalic acid to the electrolyte. Since the decomposition of the ammonium oxalate occurs more rapidly in hot solutions, it is always preferable to carry out the electrolysis in cold solutions, with current densities of from 1 to 1.5 ampères.

In order to ascertain if the whole of the iron has been removed from the solution, a few drops are withdrawn by means of a small pipette, and to this, after acidifying with hydrochloric acid, a small portion of sulphocyanide of potassium solution is added. A red coloration of the mixture denotes the presence of iron, and occurs with extremely small amounts of this metal. If it be found that all the iron is deposited, the liquid is poured out of the basin, or the jacket electrode is raised out of the solution, the deposit and its support are rinsed several times with water, then with alcohol, and are finally dried in the air bath at 100°C .

The deposit of iron should be of a bright steel-grey colour.

Ferric salts may be treated in an exactly similar way, but in the case of these it is unnecessary to take any precautions in mixing the iron and ammonium oxalate solutions. The difference in colour between the complex double oxalates of iron and the simple salts of iron are worthy of notice. While the latter give for ferrous salts green solutions, and for ferric salts solutions reddish brown in colour, the ferrous double oxalate yields a red and the ferric double oxalate a green solution.

When the ferric salts are electrolysed as double oxalates, the colour of the solutions changes from green to red, and the red gradually fades away to a complete absence of any colour whatever. Ferric potassium sulphate (iron alum), $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 + 24\text{H}_2\text{O}$, or ferric potassium oxalate, $\text{Fe}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{K}_2\text{C}_2\text{O}_4 + 6\text{H}_2\text{O}$, may be used as ferric salts, or one may use the ordinary hydrated ferric chloride. The chlorides may in fact be safely used when employing this method of electrolysis of double oxalates; but nitrates must be avoided, since their use almost invariably occasions a separation of ferric hydrate. If therefore the nitrate salts are to be analysed, it is best to convert them into sulphates by heating with excess of sulphuric acid. The chief portion

of the excess must be removed by evaporation, and the remainder is then neutralised by ammonia.

For the electrolysis of iron, besides the double oxalate salts, solutions containing citrates and tartrates of the alkali metals have been recommended and used by Smith.¹ A solution containing 1 grm. of ferrous sulphate is treated with 2 to 3 grms. of ammonium citrate and a small amount of citric acid, and is then electrolysed with a current of from .7 to 1 ampère in density.² It is possible to obtain bright deposits of iron in this way, but on dissolving the deposit in dilute sulphuric acid, particles of carbon will be detected; and this is especially the case when high current densities have been employed for the deposition of the iron. As a consequence of this, the results obtained are too high.

The separation of iron from this solution also occurs very slowly, six to seven hours being necessary to deposit the iron contained in 1 grm. of ferrous sulphate.

Solutions containing the tartrates of the alkali metals behave similarly. For example, a complete separation of the iron is possible from an ammonium tartrate solution,³ but the deposit contains carbon. Luckow has recommended the ammonium fluoride double salt.⁴

Moore has proposed solutions containing sodium phosphate,⁵ Brand solutions containing pyrophosphates of the alkali metals,⁶ for use in obtaining deposits of iron. These solutions demand a very high E.M.F., and much time for their decomposition; and the deposits obtained are not very good.

[Nicholson and Avery have suggested an improvement of Classen's oxalate method by the addition of sodium borate to the ferrous ammonium oxalate solution.⁷—*Translator's note.*]

¹ *Amer. Chem. Jour.* **10**, 330.

² v. Müller and Kiliani, *Lehrbuch der Analyse*.

³ *Jour. Anal. and Appl. Chem.* 1891, **5**, 488.

⁴ *Zeitschr. f. anal. Chem.* **19**, 1.

⁵ *Chem. News*, 1886, **53**, 209.

⁶ *Zeitschr. f. anal. Chem.* **28**, 581.

⁷ *Jour. Amer. Chem. Soc.* **18**, 654.

The method which depends upon the use of the double oxalate salts is the only simple and safe one to employ for the analytical electrolysis of solutions of iron. This method has been used in determining the atomic weight of iron. For technical purposes the electrolytic determination of iron is of little importance, since it is unlikely to be used in place of the volumetric method with permanganate of potash. It may, however, be employed in standardising such solutions of permanganate.

NICKEL

Nickel, like iron, is one of that group of metals which are not separated by the customary currents of from 1 to 2 ampères from strongly acid solutions. The separation from neutral salt solutions is only incomplete. Luckow, however, states¹ that this drawback is avoided by the addition of a small quantity of acetic acid, and Riche states² that the same effect is produced by other acids. The method proposed by Gibbs,³ and by Fresenius and Bergmann,⁴ depends upon the use of a solution containing free ammonia and ammonium sulphate, and this has proved to be the most convenient and neat. Either the sulphate or chloride of nickel may be employed. A solution of 1 grm. of nickel sulphate in a little water is prepared, and to this a solution of from 5 to 10 grms. of ammonium sulphate is added, together with 30 to 40 c.cms. of ammonium hydrate.

This solution is electrolysed at the normal temperature, with a current density of .5 to 1.5 ampères and an E.M.F. of 2.8 to 3.3 volts. The deposition will be complete in about two hours. If the solution be heated to 50° to 60° C. the deposition can be effected in fifty to sixty minutes, by use of a current density of 1.5 ampères and an E.M.F. of 3.4 to 3.8 volts. The deposit obtained is bright and shining, and resembles in appearance rolled platinum; and it is to some extent proof against the action of dilute acids.

¹ *Zeitschr. f. anal. Chem.* 1880, 19, 1.

² *Ibid.* 21, 116.

³ *Ibid.* 1864, 3, 334.

⁴ *Ibid.* 1880, 19, 320.

This method can be employed for solutions containing a larger amount of nickel than that given above. Care must, however, be given to the maintenance of an excess of ammonium hydrate in such cases, as when this is not present, a coating of nickel, bad in colour, is obtained, and a crusting of black nickel oxide forms upon the anode. Too great an excess of ammonia retards the deposition. The metal separated from these solutions is silver-grey in colour, and adheres firmly to the kathode. Winkler¹ states that large amounts of nickel may be deposited in this way. The last traces of nickel, as in the case of iron, are difficult to separate from the solution. On this account it is not advisable to work with currents of less than 1 ampère in density, or, in case such weaker currents have been used, it is necessary to increase the density to 1 ampère towards the end of the electrolysis, and to allow this current to pass through the solution for a period of from fifteen to thirty minutes.

In order to satisfy oneself that all the nickel has been deposited, a few drops of electrolyte are tested by means of an ammonium sulphide or sodium sulphide solution. The formation of a brown colouring in the mixture is proof of the presence of nickel. Potassium sulphocarbonate may also be employed for this purpose; in this case the presence of nickel causes a rose-red coloration to appear. When it has been proved that all the nickel is deposited, the removal of the electrolyte and the washing of the deposit are effected without breaking the circuit in the manner described under Copper. The electrode and its deposit are then washed with water and alcohol, and dried at 100° C. As already remarked, the metallic coating of nickel obtained in this way possesses the noteworthy property of being but slowly attacked by sulphuric or hydrochloric acids. On this account it is best to use nitric acid for removal of the deposit from the electrode. This method for the separation of nickel always gives reliable and good results. The nitrate salt interferes with the satisfactory course of the electrolysis,

¹ *Zeitschr. f. anorg. Chem.* 1894, 8.

so that it is necessary, when this salt is to be analysed, to convert it into the sulphate by means of sulphuric acid.

It has frequently been asserted that the presence of chlorides—as, for example, ammonium chloride—has also a disadvantageous influence upon the separation of nickel. Oettel has contradicted this,¹ and has shown that useful deposits of nickel may be obtained from chloride solutions, when attention is given to the following points. The nickel chloride solution must be strongly alkaline ; at least 10 per cent. of ammonium hydrate (sp. gr. $\cdot 92$) being required in the solution to prevent the separation of the black nickel oxide at the anode.

In addition to this, at least sufficient ammonium chloride must be present to form the double chloride of nickel and ammonium ; a larger amount is not injurious, but such an addition of ammonium chloride only compensates for a shortness of ammonium hydrate when high current densities are employed. Insufficiency of ammonium hydrate increases the time required for the separation, and also the danger that the nickel may be partly separated as oxide. In order to carry out an electrolysis by this method, 1 gm. nickel chloride and 2 to 4 grms. ammonium chloride are dissolved in 100 c.cms. water, 40 c.cms. ammonium hydrate are added, and the solution is electrolysed at the normal temperature with a current density of $\cdot 5$ ampère. The deposition of the nickel is complete in four to five hours.

Larger amounts of nickel can also be obtained as firmly adhering deposits by use of this solution. Thus 1 gm. nickel may be completely deposited under the above conditions in six to seven hours, or with a current density of $\cdot 11$ ampère in fourteen hours. When using a flat kathode of sheet metal, Oettel recommends the use of a fork-shaped anode, in order to obtain an equal current density upon the two sides of the kathode, which is fixed in the centre of the anode. Although this arrangement was originally suggested for nickel deposition, it is one which can be recom-

¹ *Zeitschr. f. Elektrochem.* 1894, 1, 194.

mended for adoption in all cases in which a metal has to be deposited upon a flat electrode. Nitrates exert a disturbing influence upon the course of this electrolysis.

Good deposits of nickel are also easily obtained by use of solutions of the double oxalates of nickel and ammonium, recommended by Classen and v. Reiss,¹ and also by Classen.²

The solution is prepared similarly to that of iron, by dissolving 1 grm. nickel sulphate in water, adding a solution of 5 to 6 grms. ammonium oxalate, and by diluting this mixture until it measures 150 c.cms.

The solution is then electrolysed with a current density of 1 ampère. If the solution be heated to 50° or 60° C. the E.M.F. required will be 2·8 to 3·3 volts, and the deposition will occupy about four hours ; if the separation be effected at the normal temperature, the E.M.F. will be increased to between 3·5 and 4·2 volts, the time to five or six hours. Equally good deposits can be obtained by the employment of weaker currents ; but it will be necessary to increase these to 1 ampère or higher towards the end of the electrolysis, in order to effect the separation of the last traces of the metal.

The nickel obtained in this way is bright and steel-grey in colour, with a reddish tinge. By this method it is unnecessary to wash out the electrolyte before breaking the circuit.

In the same manner that solutions of the neutral nickel salts to which oxalates of the alkali metals have been added are used for obtaining useful deposits of nickel, solutions of neutral nickel salts containing tartrates, citrates, and acetates of the alkali metals have been proposed by Luckow,³ Wrightson,⁴ Ohl,⁵ Schweder,⁶ and Smith and Muhr.⁷ Good metallic deposits are obtained ;

¹ *Berichte*, 1881, 14, 1622.

² *Zeitschr. f. Elektrochem.* 1894, 1, 280 ; *Berichte*, 27, 2072.

³ *Dingl. polyt. Jour.* 117, 225.

⁴ *Zeitschr. f. anal. Chem.* 15, 300.

⁵ *Ibid.* 18, 523.

⁶ *Ibid.* 16, 344.

⁷ *Jour. Appl. Chem.* 1891, 5, 488 ; 1893, 7, 189.

but when using the tartrates and citrates, there is the same tendency, observed with iron, for carbon to be deposited with the metal. Solutions containing an excess of potassium cyanide may also be used for nickel deposition, according to Ohl,¹ Schweder,² Wrightson,³ and Luckow.⁴ The author has obtained, however, under the most varying condition, only dark-coloured non-adherent deposits from this solution. Von Foregger⁵ states that useful deposits of nickel may be obtained from solutions of nickel salts to which ammonium carbonate has been added. To prepare such a solution 1 grm. nickel sulphate and about 15 grms. ammonium carbonate are dissolved in 150 c.cms. water. This is heated to 50° or 60° C., and a current of from 1·0 to 1·5 ampère intensity is used to decompose it, with an E.M.F. of 3·5 to 4·0 volts.

The complete separation of the nickel in the usual bright metallic form will be effected in 1½ hrs. Useful deposits of nickel can be obtained from solutions that have merely received an addition of 10 c.cms. of ammonium hydrate, on electrolysing them at the normal temperature with currents of from ·1 to ·5 ampère in density.

Similar results can be obtained from solutions containing an excess of pyrophosphoric acid and ammonium carbonate. A solution of nickel sulphate is treated with 25 c.cms. ammonium hydrate and 25 c.cms. of a saturated solution of sodium pyrophosphate ; this is then electrolysed, either at the normal temperature or after heating. With a current of from ·3 to ·5 ampère the deposition will occupy sixteen hours, with ·5 to ·8 ampère, nine hours.

Stronger currents may also be employed.

The deposits obtained are good, but the deposition takes place too slowly, and the solution has a tendency to permit nickel oxide to separate at the anode.

[Nicholson and Avery have recommended the use of

¹ *Zeitschr. f. anal. Chem.* 17, 215.

² *Ibid.* 16, 344.

⁴ *Ibid.* 19, 1.

³ *Ibid.* 15, 300.

⁵ *Dissertation*, 1896, Berne.

solutions containing the metal as sulphate, with addition of ammonium oxalate and sodium borate—an improvement of Classen's oxalate method.¹—*Translator's note.*]

The method which finds frequent and exclusive employment in technical laboratories is that first described, depending upon the use of ammonium hydrate and ammonium sulphate. Nevertheless, the methods in which ammonium chloride, ammonium oxalate, and ammonium carbonate are used may occasionally be employed with advantage.

COBALT

Cobalt so closely resembles nickel in most of its properties, that those electrolytic methods which are found useful for separating nickel are also applicable for cobalt. In most cases the proposals made by various experimenters for the deposition of nickel cover at the same time that of cobalt.

To carry out an electrolytic determination of cobalt, 1 grm. cobalt sulphate and 5 grms. ammonium sulphate are dissolved in 100 to 120 c.cms. water, and 30 to 40 c.cms. ammonium hydrate are added. This solution is then electrolysed with a current density of from .5 to 1.5 ampère, either at the normal temperature or at 50° to 60° C.

The E.M.F. and time required for this deposition are practically the same as in the case of nickel; and ammonium sulphide or potassium sulphocarbonate is likewise used to determine the completion of the deposition. Nitrates produce a disturbing effect upon the electrolysis. The remarks made under 'Nickel' regarding the use of the chloride with ammonium chloride are also correct for cobalt; but as cobalt is in general more difficult to separate from its solutions than nickel, it is necessary to use a weight of ammonium chloride equal at least to four times that of the cobalt present; and the ammonium hydrate added must equal one-fifth of the total volume of the liquid. The electrolysis requires less time the greater the proportion of ammonium hydrate present in the electrolyte.

¹ *Jour. Amer. Chem. Soc.* **18**, 654.

The solution is therefore made up as follows : 1 gram. cobalt chloride and 5 grms. ammonium chloride are dissolved in water, and the solution, after addition of 30 c.cms. ammonium hydrate, is made up to 150 c.cms. It is then electrolysed with a current density of 1.5 ampères. The time required to complete the separation is five to six hours ; and as a general rule it is more difficult to remove the last traces of cobalt from the solution than those of nickel.

The method with solutions of the double oxalates gives equally good results with salts of cobalt as with those of nickel. The colour of the deposit of cobalt is slightly different to that of the deposit of nickel ; but the metallic coat is equally bright. The separation from a solution containing 1 gram. cobalt sulphate and 5 to 6 grms. ammonium oxalate in 150 c.cms. water is complete in four hours, when the electrolysis is conducted at a temperature of 50° to 60° C. ; at the normal temperature six to seven hours are requisite to complete the deposition. The E.M.F. in the former case is from 3.2 to 3.8 volts ; in the latter, 3.8 to 4.2 volts.

When small currents have been used to effect the separation, an increase of the current-strength is absolutely necessary in order to remove the last traces of the metal from the solution.

The method with ammonium carbonate has also been suggested by von Foregger for use with cobalt salts.¹

Quantitatively exact results are obtained, but the metal deposit is not so bright as that obtained when using the first method described. The solution is prepared by dissolving 1 gram. cobalt sulphate and 15 grms. ammonium carbonate in water, adding a few cubic centimetres of ammonium hydrate, and making up to a volume of 150 c.cms. by addition of water. This solution is then heated to 50° or 60° C., and is electrolysed with a current density of 1 ampère. The E.M.F. required is from 3.7 to 3.9 volts ; the time varies between $2\frac{1}{2}$ and $3\frac{1}{2}$ hours.

From solutions containing an excess of potassium

¹ *Dissertation*, 1896, Berne.

cyanide a quantitative separation of cobalt is no more possible than in the case of nickel, in many cases cobalt oxide separating at the anode.

The method with the pyrophosphates of the alkali metals gives the same results as with nickel.

A cobalt solution containing 3 grms. sodium pyrophosphate and 100 grms. ammonium hydrate requires seven hours for the separation of .1 to .2 grm. of the metal, and is therefore unfitted for practical use.

The method with ammonium sulphate and ammonium hydrate is that which alone finds employment in actual practice; though, as regards the other methods, the remarks made upon this point under 'Nickel' are also true for cobalt.

If a solution contains both nickel and cobalt, all the methods described above will lead to a simultaneous separation of the two metals at the kathode.

ZINC.

Zinc belongs—in accordance with its position in the voltaic series of metals—to the same group as iron, nickel, and cobalt; that is to say, the quantitative separation of zinc from solutions containing more than a very small percentage of free acid is not possible by the ordinary current intensity.

In many respects zinc behaves similarly to the metals whose separation has been already described, but it differs from these in its tendency to separate in the spongy form. Such spongy deposits are obtained especially by the electrolysis of neutral salt solutions; and in order to avoid this objectionable feature Reinhardt and Ihle have recommended the addition of a small amount of acetic acid to the electrolyte,¹ while Luckow (*l.c.*), Parrodi and Mascazzini,²

¹ *Jour. f. prakt. Chem.* **24**, 195.

² *Gazz. chim. Ital.* **1877**, iv. v. 222; *Berichte*, **10**, 1098.

Riche,¹ Millot,² Reinhardt and Ihle,³ and Rüdorff⁴ have recommended the addition of sodium acetate for the same purpose. Neither of these additions, however, effectually prevents the occurrence of spongy deposits. It is necessary to note here that the deposition of zinc upon the usual platinum electrodes leads to unpleasant results ; for on dissolving the dried and weighed deposit of zinc a black powdery coat remains, as a rule beneath the whole of the deposit but at least about the edges of the electrode, which is neither soluble in hot hydrochloric acid nor in hot nitric acid.

Vortmann states that this black coat consists of finely divided platinum,⁵ and that a mere mechanical rubbing with sand will remove it. This is of course an objectionable treatment for the platinum electrode. On this account it is customary to coat the electrode which is to serve as kathode with some other metal before its use for zinc depositions. Copper, silver, or tin is most generally used for this purpose.

The procedure described under 'Copper,' in which nitric acid is used in the electrolyte, is especially suitable for obtaining such a coating of copper. The current is only allowed to pass for a few minutes ; the electrode is then washed, dried, and weighed. This coating of other metal, used to protect the platinum of the electrode, may lead to incorrect results during the after electrolysis of the zinc salt, owing to minute drops of the electrolyte being carried or spirted, by the bubbles of gas which escape from the liquid, on to the portion of the coating which is not immersed. The copper may in this way be oxidised ; the other metals may even be dissolved. To guard against this source of error, the coating upon the inner surface of the basin, or upon the jacket electrode, is made only very slightly higher than the level to which the electrolyte will reach.

¹ *Compt. rend.* **85**, 226 ; *Zeitschr. f. anal. Chem.* **17**, 218.

² *Bull. de la Soc. Chim.* 1882, **37**, 339.

³ *Jour. f. prakt. Chem.* **24**, 195.

⁴ *Zeitschr. f. angew. Chem.* **1892**, 179.

⁵ *Berichte*, **24**, 2753.

This is most simply attained by measuring the volume of the zinc solution of which the electrolysis is to be made, and by using a volume of silver or copper solution 5 to 10 c.c. greater.

In order to avoid the trouble involved in preparing these coatings, nickel basins or jacket electrodes have been used. These are of course subject to the action of the acid when the zinc is dissolved.

The zinc deposit obtained from any solution is only fitted for analytical work when it is of a pale greyish-blue colour, and is firmly adherent to the kathode.

Dark deposits are to be regarded with distrust, while deposits which are partly or wholly spongy in character must be rejected. At the commencement of the electrolysis most solutions yield a deposit of the desired character, but it is from a few only that absolutely trustworthy deposits can be obtained when the electrolysis lasts for a considerable period of time.

One of these latter is the solution of the double cyanide of zinc and potassium, recommended by Luckow,¹ Beilstein and Jawein,² and Millot.³

The solution for electrolysis is prepared by dissolving 1 grm. zinc sulphate in a little water, and by adding to this a solution of pure potassium cyanide in small portions at a time, until the precipitate of zinc cyanide, which first forms, has dissolved in the excess of potassium cyanide.

If other salts of zinc containing free acid be used, it is necessary to neutralise this acid with sodium hydrate, or to make the solution slightly alkaline before adding the potassium cyanide.

The clear colourless solution of the double cyanide is made up to 150 c.cms., and may be electrolysed with either strong or weak currents, at the normal or at a higher temperature. Under all conditions and without any attention, it yields on electrolysis, homogeneous, pale blue

¹ *Zeitschr. f. anal. Chem.* 19, 1.

² *Berichte*, 12, 446.

³ *Bull. de la Soc. Chim.* 1882, 37, 339.

deposits of zinc which are firmly adherent to the kathode.

At the normal temperature an E.M.F. of 5.8 volts will be required for a current of .5-ampère density, but this E.M.F. will fall during the electrolysis owing to the heating of the electrolyte by the current. The deposition will occupy between two and two and a half hours.

If the electrolysis be conducted at 50° C., the E.M.F. required is reduced to 5 volts and the time to two hours for the above current density. It is possible to obtain equally good deposits when using a current density of 1 ampère ; in this case, at a temperature of 50° to 60° C., all the zinc is deposited in from an hour and a half to an hour and three-quarters with an E.M.F. of from 5 to 5.2 volts.

This method with the double cyanide of potassium and zinc is also adapted for obtaining depositions during the night with weak currents.

The recognition of the complete deposition of the zinc is attained by use of potassium ferrocyanide solution.

The presence of zinc is proved by the formation of a white insoluble precipitate, insoluble in hydrochloric acid, or a white cloudiness of ferrocyanide of zinc. In order to apply this test, the small test-portion of the electrolyte—the withdrawal of which demands care, lest any should be sucked into the mouth—is treated with a few drops of hydrochloric acid, and after warming is mixed with potassium ferrocyanide.

For some solutions which are already alkaline, or the test-portion of which has been made so by the addition of ammonia, sodium or ammonium sulphide solution may be used to determine the presence of zinc. In this case white zinc sulphide is formed.

When the deposition has been proved to be complete, the cone is removed from the solution, or the basin is washed out before breaking the circuit, and the deposit of zinc is washed with water and alcohol and dried in the air-

bath at 100° to 110° C., as previously described. The deposit should be of a pale greyish-blue colour.

Reinhardt and Ihle¹ and Classen and v. Reiss² have recommended the use of the double oxalates for obtaining useful deposits of zinc. In order to prepare such a solution 1 gram. zinc sulphate is dissolved in water, and to this is added a solution containing 4 grms. ammonium oxalate. The precipitate of zinc oxalate which first forms dissolves in the excess of ammonium oxalate, which is present in much greater amount than that requisite to form the double salt. This neutral solution may be electrolysed at the normal temperature with a current density of .5 ampère. An E.M.F. of from 3.8 to 4.1 volts will be required, and the deposition will be completed in about four hours.

With smaller amounts of zinc, and current densities which do not exceed .5 ampère, it is possible to obtain bright deposits ; but spongy deposits under these circumstances may also occur.

Similar results are obtained by use of the potassium zinc oxalate salt recommended by Reinhardt and Ihle,¹ and by v. Miller and Kiliani.³ This solution is prepared by dissolving 1 gram. zinc sulphate, 4 grms. potassium oxalate, and 3 grms. potassium sulphate ; the best results are obtained when it is electrolysed at the normal temperature with a current density of .3 ampère. The E.M.F. required is from 3.9 to 4.2 volts, and the time from three to four hours. Classen has shown that in order to obtain with certainty reliable deposits of zinc from the solutions of the double oxalates, it is absolutely necessary to maintain the electrolyte acid during the electrolysis, by means of the addition of small amounts of free organic acids.⁴ Either oxalic, tartaric, or lactic acid may be used for this purpose. It is most convenient to use a 5 per cent. solution of tartaric acid, which is less readily decomposed than oxalic acid ; 1 to 2 c cms. of this solution are added to the

¹ *Jour. f. prakt. Chem.* **24**, 195.

² *Berichte*, 1881, **14**, 1630.

³ *Quant. Analyse*.

⁴ *Zeitschr. f. Elektrochem.* 1894, **1**, 280.

ammonium zinc oxalate solution prepared as described above, at the commencement of the electrolysis.

During the deposition of the zinc small amounts continue to be added, and tests with litmus paper are made in order to have proof that the electrolyte has been kept acid. Too great an excess of acid delays the deposition. By use of this method dense and bright deposits of zinc can be obtained ; but the electrolysis demands some attention during its course. The ammonium zinc oxalate solution is best electrolysed at a temperature of 50° to 60° C. with $\cdot 5$ ampère ; the E.M.F. required will be from 3·5 to 4·0 volts, and the time two hours. When 1 ampère is used, the E.M.F. rises to between 4·7 and 4·8 volts, and the time is reduced to an hour and a half. The deposit obtained is pale bluish-grey in colour. If the electrolyte has not been kept acid during the electrolysis, grey zinc sponge is nearly always formed.

When tartaric acid has been used as recommended above, in order to maintain the electrolyte in the acid state the test with potassium ferrocyanide is not applicable. It is necessary to wash the electrolyte from the basin or cone before breaking the circuit, when using this method with the double oxalates.

Jordis has shown that good deposits can be obtained when ammonium lactate and free lactic acid are used in place of ammonium oxalate and oxalic or tartaric acid.¹ The solution is prepared by dissolving 1 grm. zinc sulphate, 2 grms. ammonium sulphate, and 6 grms. ammonium lactate in 150 c.cms. water, and by adding to this solution 10 drops of lactic acid.

The electrolysis may be carried out with current densities varying between $\cdot 5$ and 1 ampère ; in the latter case, with solutions heated to 50° to 60° C., the deposition occupies an hour and a half, while the E.M.F. required is from 3·8 to 4·5 volts.

The zinc deposit obtained is pale blue. It would be

¹ *Zeitschr. f. Elektrochem.* 1895, 2, 656.

erroneous to draw the conclusion, from the similarity which in other respects exists between zinc, and cobalt or nickel, that the solution of the double sulphate of ammonium and zinc, to which excess of ammonium hydrate has been added, will yield good deposits of zinc. A solution containing 1 grm. zinc sulphate and 6 grms. ammonium sulphate, with a small addition of ammonium hydrate, will give bright deposits under certain conditions with weak currents. From neutral solutions of zinc ammonium sulphate it is possible to separate all the zinc contained in 1 grm. zinc sulphate with a current density of from $\cdot 3$ to $\cdot 5$ ampère in an hour, as a rule, in a useful form ; but occasionally the deposit is spongy. The E.M.F. required varies between 3 and 4 volts.

The presence of chlorides or of ammonium hydrate in the electrolyte increases, as a general rule, the tendency to form spongy deposits.

The use of zinc sulphate solutions to which sodium or ammonium acetate and free acetic or citric acid have been added has been proposed by Riche,¹ Rüdorff,² and Parrodi and Mascazzini.³ 1 grm. zinc sulphate and 3 grms. sodium acetate are dissolved in water in order to prepare such a solution, and 20 drops of acetic acid are added.

In order to electrolyse this solution at the normal temperature with a current of $\cdot 5$ ampère, an E.M.F. of from 5·9 to 6·3 volts is required.

The deposit, which is at first bright, becomes later spongy in character ; if a current of only $\cdot 2$ to $\cdot 3$ ampère be, however, employed, a useful deposit can be obtained ; the time required will be about eight hours. If such a solution be heated to 50° or 60° C., and a current of $\cdot 5$ ampère be again used, a good deposit of zinc, bluish-white in colour, can be obtained. The E.M.F. required will in this case be reduced to about 5 volts, and the time required will be between three-quarters and one hour.

¹ *Compt. rend.* **85**, 226 ; *Zeitschr. f. anal. Chem.* **17**, 208.

² *Zeitschr. f. angew. Chem.* **1892**, 179.

³ *Gazz. chim. Ital.* **1877**, iv. v. 222 ; *Berichte*, **10**, 1098.

Insufficiency of acetic acid increases the tendency to form a spongy deposit ; it should therefore be added in small portions at a time during the electrolysis. Excess of this acid delays the deposition. It is necessary to wash without breaking the circuit, when using this method. This electrolysis yields precisely similar results when ammonium acetate is used, in place of sodium acetate, with the zinc sulphate solution. In order to prepare such a solution 1 gm. zinc sulphate is dissolved in water, and ammonium hydrate is added until the precipitate which first forms has redissolved. Acetic acid is now added until a feebly acid reaction is produced. From this solution, heated to 50° or 60° C., the zinc can be wholly deposited in about an hour by use of a current of .5 ampère. An E.M.F. of from 3.5 to 4 volts is required. The deposit is bright and firmly adherent to the electrode.

Vortmann has recommended the use of zinc solutions containing tartrates of the alkali metals.¹ The solution of zinc sulphate is prepared in this case for electrolysis by adding 5 to 6 grms. sodium potassium tartrate and 2 to $2\frac{1}{2}$ grms. caustic soda, and it is then electrolysed at the normal temperature with a current of from .40 to .70 ampère in density. The complete deposition requires from two to three hours ; the character of the deposit obtained is satisfactory.

If an excess of sodium hydrate solution be added to a solution of a zinc salt, a solution of sodium zincate is formed, which has also been recommended for electrolysis by Millot² and Kiliani and v. Foregger.³ This solution does not give bright deposits in all cases.

Satisfactory results may be obtained if solutions of 1 gm. zinc sulphate and from 2.5 to 4.0 grms. caustic soda are mixed, and, after dilution and heating to 50° to 60° C., are electrolysed with currents of from .70 to 1.5 ampères

¹ *Monats. f. Chem.* 1893, **14**, 546.

² *Bull. de la Soc. Chim.* 1882, **37**, 339.

³ *Dissertation*, 1896, Berne.

in density. The E.M.F. required is from 3·9 to 4·5 volts ; complete deposition is effected in two hours. Increase in the amount of caustic soda improves the character of the deposit.

Solutions containing sodium or ammonium chloride give, under certain conditions, good deposits ; but on account of the unpleasant nature of the gas liberated at the anode—chlorine—they are but little used. Little use is also made of a solution which contains only 10 c.cms. ammonium hydrate in addition to the zinc salt.

In this latter case a current of from ·10 to ·30 ampère in density requires five to six hours to complete the deposition of the zinc.

Other additions that have been suggested are ammonium phosphate, by Moore,¹ and sodium pyrophosphate and ammonium carbonate, by Brand.² Solutions prepared with these salts seldom give good deposits. [Nicholson and Avery recommend the use of zinc solutions containing the metal as sulphate with the addition of formic acid in excess, and sodium hydrate.³—*Translator's note.*]

The traces of zinc that remain in the electrolyte towards the end of the electrolysis of zinc salt solutions are very difficult to remove. In this respect zinc resembles iron and nickel. In order to effect their deposition, it is necessary towards the end of the electrolysis to increase the current density if this be feasible, or otherwise to allow the current to continue to pass through the electrolyte for a fairly long period of time.

In technical laboratories the electrolytic methods of determining zinc are little used ; this is especially true of those laboratories in which a large number of zinc estimations have to be made concurrently. This does not signify, however, that in particular instances the electrolytic methods are not the most suitable. When these methods

¹ *Chem. News*, 1886, 53, 209.

² *Zeitschr. f. anal. Chem.* 28, 581.

³ *Jour. Amer. Chem. Soc.* 18, 654.

are employed, that first described with the double cyanide of zinc and potassium is the most to be recommended, since it yields with certainty good deposits, and permits the use of fairly strong currents.

CADMIUM

This metal is closely related to zinc, not only in its electrical but in its chemical and other properties. Like iron, nickel, and zinc, it cannot be deposited from strongly acid solutions, and it especially resembles the latter metal in the tendency that it exhibits, even more strongly than zinc, to separate in a spongy or loose form. The presence of from $1\frac{1}{2}$ to 2 per cent. mineral acid in the solution completely stops the deposition. Bright silvery white metallic deposits can only be obtained with regularity from comparatively few solutions; and the amount of the metal which can be separated in this form is, further, very limited.

For these reasons it is especially necessary, in the electrolysis of cadmium salt solutions, to take great care that the electrodes are perfectly clean, and also that the form of the electrodes used for carrying out the electrolysis is such that the current density will be practically the same at all points of the kathode surface. The electrodes are most satisfactorily cleaned by boiling with acids or by immersion in fused potassium bisulphate.

One of the best deposits of cadmium is obtained by the electrolysis of the double cyanide of cadmium and potassium, as recommended by Beilstein and Jawein¹ and by Wallace and Smith.²

This electrolysis is carried out in the same manner as that of the corresponding salt of zinc. 50 gm. cadmium sulphate is dissolved in water, and to this solution pure potassium cyanide solution is added until the first-formed precipitate of cadmium cyanide has redissolved. The solution is then diluted to 150 c.cms., and is electrolysed at the

¹ *Berichte*, 1879, 12, 446.

² *Ibid.* 1892, 25, 779.

normal temperature with a current of $\cdot 50$ ampère. The E.M.F. required will be from 4.75 to 5.0 volts, and the time from six to seven hours. The presence of an excess of potassium cyanide in the solution is advisable, in order to lessen the tendency to form a spongy deposit.

In order to test whether the deposition is complete, sulphuretted hydrogen is used with a feebly acid test-portion of the electrolyte. A yellow precipitate or a yellow colouring of the solution indicates the presence of cadmium. When the electrolyte contains cyanides, as in the above case, it is first necessary to destroy these by boiling the test-portion with excess of dilute sulphuric acid (under a draught-hood); the solution is then nearly neutralised, and sulphuretted hydrogen gas is passed through it.

Good deposits may also be sometimes obtained by use of neutral salt solutions; but it has been found that the deposits are denser and show less tendency to a spongy formation if some free acid be added to the liquid during the electrolysis. Luckow¹ and Smith² have recommended sulphuric, nitric, or acetic acid for this purpose; while Warwick³ has recommended formic acid.

The solution of $\cdot 30$ gram. cadmium sulphate in 150 c.cms. water receives an addition of from 1 to 2 c.cms. of dilute sulphuric acid, and after heating to 70° or 80°C . is electrolysed with a current of from $\cdot 60$ to 1.0 ampère. The E.M.F. required to produce this current varies between 2.5 and 5.0 volts according to the amount of free acid present; the deposition demands three hours. A silver-white deposit is obtained.

Heydenreich⁴ has stated that a solution of $\cdot 30$ gram. cadmium sulphate containing free acetic acid yields, with currents of from $\cdot 10$ to $\cdot 40$ ampère in density, a bright deposit of a crystalline lamellar character, and not particularly

¹ *Zeitschr. f. anal. Chem.* 19, 1.

² *Chem. Jour.* 10, 330.

³ *Zeitschr. f. anorg. Chem.* 1, 285.

⁴ *Zeitschr. f. Elektrochem.* 1896, 3, 151.

adherent to the kathode. The E.M.F. required is from 4·5 to 7·5 volts.

Solutions made alkaline with ammonium hydrate cannot be recommended for use ; the metal separates in the spongy form, even after addition of ammonium sulphate.

Classen and v. Reiss¹ found that good results could be obtained by use of the double oxalate salt of cadmium and ammonium. The whole of the metal can be deposited from a solution containing ·30 grm. cadmium sulphate and from 8 to 10 grms. ammonium oxalate, with a current of ·60 ampère, in about two hours.

At a temperature of 50° to 70° C., the E.M.F. required is from 2·7 to 3·4 volts. The deposit is bright and firmly adherent to the electrode.

The addition of a little free acid to the electrolyte is found (as in the case of zinc) to increase the density of the deposited metal, and to lessen the tendency to sponge formation even at higher current densities. In order to carry out the electrolysis in this way, the solution of the double salt, as described above, is again prepared, and during the electrolysis of the hot solution a few cubic centimetres of an oxalic acid solution are added from time to time, so that the electrolyte is kept slightly acid.

Tartaric acid, which is more stable than oxalic acid, may be used with equally good results.

The current density can, under these conditions, be allowed to vary between ·50 and 1·5 ampère without any danger to the character of the deposit. The E.M.F. required for a current of from ·60 to ·70 ampère at 70° C. is between 2·7 and 3·2 volts, and the time about three hours and a half ; while for 1 ampère the E.M.F. is between 2·75 and 3·3 volts, and the duration of the electrolysis about three hours. When tartaric acid has been used to acidify the electrolyte, the E.M.F. required is slightly increased, being from 3·0 to 3·4 volts ; while the deposition takes place rather more slowly, and on this account less close attention is necessary.

¹ *Berichte*, 1881, 14, 1622.

V. Miller and Kiliani have recommended the use of solutions containing sodium acetate and free acetic acid for cadmium depositions.¹

Such a solution is prepared by dissolving .50 grm. cadmium sulphate and 3.0 grms. sodium acetate in water and mixing the solutions. A little free acetic acid is added to the mixture, and after diluting and heating to 50° C. it is electrolysed with a current of from .20 to .70 ampère. The complete separation of the metal from this solution requires between five and eight hours. The current densities which may be safely employed in this method are too small for practical work ; and there is the further disadvantage, noticed by the authors, that the deposit has a tendency to pass into the spongy form.

Moore has found that solutions of cadmium to which sodium phosphate and phosphoric acid have been added, yield non-metallic deposits unfitted for quantitative work.² If, however, the cadmium be precipitated from its solution by means of a solution of sodium pyrophosphate, and the precipitate be dissolved in an excess of ammonium hydrate, the electrolysis of this solution with currents of from .10 to .30 ampère will yield useful deposits.

Warwick has recommended the use of the double salt of cadmium and sodium or potassium formate ;³ while Smith and Moore have suggested the double tartrate.⁴

These solutions, however, like those that have just received notice, are not adapted for the requirements of practical work.

Solutions of cadmium salts containing free ammonium hydrate give in nearly every case spongy deposits. Deposits which are not firmly adherent, and of a dead silver-white colour, cannot be trusted to yield exact results.

The determination of cadmium is not of frequent

¹ *Lehrbuch der Analyse.*

² *Chem. News*, 1886, 53, 209.

³ *Zeitschr. f. anorg. Chem.* 1, 285.

⁴ *Jour. Anal. and Appl. Chem.* 1893, 7, 189.

occurrence in technical laboratories ; and up to the present the electrolytic methods have not been used, because the deposition has not been satisfactorily complete and the amount of the metal which could be obtained in compact and adherent form was too small. There is, however, no longer cause for the exclusion of the electrolytic methods for determining cadmium from the technical laboratory, as the result obtained by use of the potassium cyanide method, and also those obtained with the solutions containing free sulphuric acid, or with the acidified solution of the double oxalates, are perfectly reliable, and the methods are easily carried out.

LEAD

Lead belongs to a group of metals, of which manganese, silver, bismuth, and thallium are the other chief members. These differ from the metals which have so far received attention, in their property of separating from many solutions in a non-metallic form.

This separation occurs as peroxide, or at least as a higher oxide, at the anode. Frequently the metal separates in the metallic form at the kathode concurrently with its deposition as peroxide at the anode.

Manganese and lead, however, differ from the other metals of the group in the ease with which it is possible to obtain the deposition of all the metal present in the electrolyte, as peroxide at the anode. The methods proposed for obtaining the quantitative separation of lead as the metal are numberless. Some of these yield unsatisfactory results, owing to the deposits of lead occurring not as uniform firmly adherent coats, but as growths of needle-like or lamellar structure, which extend out toward the anode and cause short circuiting in the electrolytic cell.

Other solutions—e.g. those of the highly complex salts—which yield the lead as homogeneous and dense deposits at the kathode, are nevertheless unfitted for use in the

quantitative determination of this metal, because after washing with water and alcohol some oxidation of the lead coating occurs during the after drying, whether this be conducted in the air-bath or in the desiccator. It is found impossible to prevent this oxidation, and its occurrence of course leads to incorrect results.

Solutions of the neutral lead salts yield deposits of lead and lead peroxide. Deposits of metallic lead alone may be obtained from the following: neutral lead acetate solution, proposed by Luckow¹ and Kiliani;² solutions containing free acetic acid, proposed by Vortmann;³ solutions containing an addition of saturated sodium chloride, suggested by Kiliani² and Becquerel;⁴ solutions to which have been added excess of sodium hydrate, recommended by Weil,⁵ Kiliani,² Schiff,⁶ Schucht,⁷ and Parrodi and Mascazzini;⁸ solutions containing an addition of tartrates or acetates of the alkali metals or of ammonium oxalate, proposed by Classen and v. Reiss;⁹ solutions to which pyrophosphates of the alkali metals have been added, as suggested by Brand;¹⁰ and, in addition to these, all solutions which suffer decomposition by means of easily oxidised (reducing) bodies. In spite, however, of the complete separation of the lead which is possible with the above solutions, they are not in use for the quantitative determination of lead.

The separation of lead as peroxide is quite as easily effected as the separation as metal; and this can rank with the very best electrolytic methods in regard to its convenience and accuracy. Luckow pointed out, so long ago as 1865, that lead could be completely separated as peroxide

¹ *Zeitschr. f. anal. Chem.* **19**, 1.

² *Berg- u. Hütten-Zeitg.* **1883**, 285.

³ *Berichte*, **24**, 2758.

⁴ *Compt. rend.* **1854**, No. 26; *Dingl. polyt. Jour.* **1854**, 213.

⁵ Tommasi, *Electrochemie*.

⁶ *Berichte*, **10**, 1098.

⁷ *Zeitschr. f. anal. Chem.* **1883**, **22**, 287.

⁸ *Ibid.* **16**, 469.

⁹ *Berichte*, **14**, 1627.

¹⁰ *Zeitschr. f. anal. Chem.* **28**, 581.

from solutions containing free nitric acid,¹ if there were at least 10 per cent. by volume of the free acid present in the electrolyte.² In order to carry out such a separation, 1 grm. lead nitrate is dissolved in a little water, from 20 to 30 c.cms. nitric acid are added, and the mixture is diluted to 150 c.cms. The cell connections are then made, care being taken that the electrode of greatest surface area—i.e. the basin or the jacket electrode—is used as *anode*. It is advantageous to employ a dulled, or at least a much-used electrode for the separation of lead as peroxide, as the deposit adheres more firmly to such than to a new and perfectly smooth surface. The current densities employed in this separation may rise to 2 ampères without injury to the deposit. With a current of .50 ampère, at the normal temperature, an E.M.F. of from 2.0 to 2.4 volts is requisite ; and between two and two and a half hours suffice to effect the complete separation of the lead as peroxide. If the solution be heated to 50° or 60° C., and a current density of 1.5 ampères be employed, the E.M.F. required will be from 2.1 to 2.5 volts, and the time will be reduced to about an hour. A higher temperature is not to be recommended, since the adherence of the deposit to the electrode is unfavourably affected by temperatures exceeding 60° C. If the amount of nitric acid present has been too small, part of the lead will be found to have separated as metal at the cathode. The deposit of peroxide is golden-yellow or reddish in colour when only small amounts of lead are present in the solution ; the deposit is, however, dark brown or black, even from the commencement, when larger amounts are present. The deposit of lead peroxide obtained in this way is not represented by the formula PbO_2 , but contains water. The deposit cannot be reduced to the anhydrous condition by drying at the usual temperature in the air-bath ; to effect this it is necessary to dry at 180° to 200° C. The weight of anhydrous peroxide found, multiplied by .866, will give the

¹ *Dingl. polyt. Jour.* 1865, 177, 178.

² *Zeitschr. f. anal. Chem.* 19, 1.

weight of metallic lead present in the salt used for the electrolysis. The deposition of the lead as peroxide cannot be effected from solutions containing chlorides.

The deposit is redissolved if the electrolysis be allowed to continue for too great a period of time ; but in all probability this only occurs when the amount of free acid present is insufficient.

In order to test whether all the lead has been deposited from the solution, the reaction with sodium sulphide or sulphuretted hydrogen gas may be used.

The test with potassium bichromate is, however, more sensitive and less troublesome. The test-portion of the electrolyte is neutralised with ammonium hydrate, acidified with acetic acid, and then treated with a solution of potassium bichromate. Mere traces of lead cause a cloudiness, or a precipitation of yellow lead chromate.

When the electrolysis is completed, the acid liquid must be washed out of the basin, if this has been used as anode, before breaking the circuit.

The deposits of the metals which have hitherto been dealt with are easily removed from the electrodes by means of nitric acid. This method is useless for deposits of lead peroxide. In order to effect the removal of these, one may either use the dilute nitric acid solution to which oxalic acid or potassium nitrite has been added, which has then been heated, or one may use the same dilute nitric acid solution with a strip of copper or zinc to form the second element of a galvanic couple.

The latter is the simpler plan, and results in the rapid solution of the deposited peroxide.

This method of determining lead as peroxide is frequently used in technical laboratories ; it is not only simpler and more accurate than the gravimetric methods of determination, but it offers the further advantage that a separation of lead from other metals is at the same time effected. This employment of the method will, however, receive a fuller notice under 'Separations' in Part III, C.

MANGANESE

This metal, which resembles iron very closely in its chemical properties, behaves on electrolysis very differently from iron, and much more resembles lead. As with the latter metal, so manganese may be separated from certain of its solutions by the current, in the form of metal; from others, as metal and peroxide; while from others it may be obtained in the form of peroxide alone.

To obtain deposits of the metal, Moore ¹ and Smith and Frankel ² have recommended the use of solutions to which potassium sulphocyanide has been added; for both metal and peroxide, Warwick has suggested the use of the acetate; ³ but the same deposits can be obtained at times from neutral salt solutions or solutions containing a small excess of nitric acid, the acid in the latter being converted into ammonia by the action of the current.

Since metallic manganese decomposes water, these proposals are of no value for the quantitative determination of the metal, for the after washing and weighing of the separated metal is quite impossible.

To obtain deposits of pure peroxide, Luckow has recommended neutral salt solutions ⁴; Rüdorff ⁵ and Riche ⁶ have suggested neutral salt solutions to which dilute sulphuric acid has been added; Luckow, ⁷ Classen and von Reiss, ⁸ Riche, ⁶ and Schucht ⁹ have proposed the same with nitric acid in place of sulphuric acid; Becquerel ¹⁰ and Classen ¹¹ the same, with acetic acid in place of the mineral acids; while Classen and von Reiss ⁸ have recommended the

¹ *Chem. News*, 1886, **53**, 209.

² *Chem. Zeitg. Rep.* 1889, **13**, 257.

³ *Zeitschr. f. anorg. Chem.* **1**, 285.

⁴ *Zeitschr. f. anal. Chem.* **19**, 1.

⁵ *Zeitschr. f. angew. Chem.* 1892, **3**, 197.

⁶ *Compt. rend.* **85**, 226.

⁷ *Zeitschr. f. anal. Chem.* **8**, 24.

⁸ *Berichte*, **14**, 1626.

⁹ *Zeitschr. f. anal. Chem.* **22**, 492.

¹⁰ *Anal. Chim. phys.* 1830, **43**, 380.

¹¹ *Zeitschr. f. Elektrochem.* 1894, **1**, 280.

double oxalate of potassium and manganese, and Brand¹ has suggested the double pyrophosphate salt. Though it is possible to obtain from all of these solutions—especially from those containing free acid—deposits of manganese peroxide, their use suffers from the disadvantage that only very small amounts can be obtained in adherent form at the anode; about .15 grm. calculated as metal. To carry out the electrolysis of one of these solutions, one may dissolve .30 grm. manganese nitrate in water, and to this solution add 2 c.cms. nitric acid. The mixture is then diluted to 150 c.cms., and is electrolysed at a temperature of 50° to 60° C. with a current density of .30 ampère. The connections must be so made that the basin or the jacket electrode functions as anode. In this case, as in that of lead, a dulled electrode surface is most suitable for the reception of the deposit. The E.M.F. required will be from 3.0 to 3.5 volts; the deposition will demand about two hours. If the amount of free acid present should exceed 3 per cent., no peroxide is formed; permanganic acid will be produced instead. During the electrolysis the nitric acid will be decomposed and partly converted into ammonia; on this account an addition of nitric acid must be made during its course. The peroxide will be found not to adhere very well to the electrode. In place of the nitrate, one may use .30 grm. manganese sulphate, the solution of which has been acidified with 10 drops of concentrated sulphuric acid. At a temperature of 60° to 70° C., a current of from .40 to .60 ampère will suffice to deposit all the manganese from this solution in three and a half or four hours. The E.M.F. required will be 4 volts. In this case there is no necessity to add sulphuric acid during the course of the electrolysis. This method gives better results than that with nitric acid, but the deposit in this case is still unsatisfactory as regards its adherence to the electrode.

Latterly acetic acid has been again recommended for employment in place of the above two acids. In order to

¹ *Zeitschr. f. anal. Chem.* 23, 581.

carry out an electrolysis with this acid, .30 grm. manganese sulphate is dissolved in about 125 c.cms. water, and 25 c.cms. 60 per cent. acetic acid is added. The acid solution is heated to 50° or 60° C., and is electrolysed with a current of .30 ampère. The E.M.F. required under these conditions will be from 4.3 to 4.9 volts, and the whole of the manganese will be separated as peroxide in from two to two and a half hours. The deposit is no better as regards adherence to the electrode than that obtained from the preceding solution.

The same results are obtained by use of a solution containing excess of sodium pyrophosphate and free ammonium hydrate. All the manganese will be deposited in about two hours with an E.M.F. of 4.1 volts and a current of .30 ampère, but in this case the deposit is just as liable to part from the electrode as in the previous examples. Additions of free tartaric, oxalic, milk, or phosphoric acids delay the deposition of the peroxide.

In order to obtain adherent deposits of larger amounts of manganese peroxide, Engels has recently suggested a method of aiding the separation by the addition of other chemicals.¹

To a solution of 1 grm. manganese sulphate in water, a solution of 10 grms. ammonium acetate and of 1.5 to 2 grms. chrome alum is added; the mixture is made up to 150 c.cms., and after heating to 80° C. it is electrolysed with a current of from .50 to .60 ampère density. Under these conditions the E.M.F. will be from 2.8 to 3.1 volts; if the current density be increased to 1.0 ampère, the E.M.F. will rise to between 3.7 and 4.1 volts. The deposition will require from an hour and a quarter to an hour and a half.

The addition of the chrome-alum solution gives to the deposit of manganese peroxide at the anode a physical character differing from that observed in deposits from acid solution. The chief distinction is that, even in comparatively large amounts, it is firmly adherent to the

¹ *Zeitschr. f. Elektrochem.* 1895, 2, 410.

anode. For still larger amounts of manganese than that named above, the addition of chrome alum must also be increased. Alcohol may be used as a substitute for chrome alum. To prepare such a solution, 50 grm. manganese sulphate and 10 grms. ammonium acetate are dissolved in water, the mixture is diluted to about 140 c.cms., and from 5 to 10 c.cms. alcohol are added.

The solution is heated to 70° to 80° C. and is electrolysed with a current density of 1 ampère.

The E.M.F. required under these conditions will be from 4.0 to 4.2 volts, and the time about an hour and a quarter.

In order to ascertain if all the manganese has been separated from the solution, the best and most sensitive test is that with lead peroxide. The reaction with ammonium sulphide is not applicable. The small test-sample of the electrolyte is heated with lead peroxide and a few drops of concentrated nitric acid. A purple coloration, due to the formation of permanganic acid, will be produced if manganese be present in the solution in even the smallest amounts.

The brown or blackish-brown deposit of manganese peroxide which has been obtained by these various methods upon the anode is no better fitted for direct weighing after drying than the deposit of lead peroxide, since it also separates in a hydrated form.

Rüdorff has stated that if the deposit of manganese peroxide be first dried over sulphuric acid and then at 60° C., it will be found to possess the constant composition represented by the formula $\text{MnO}_2 + \text{H}_2\text{O}$.

Gröger has, however, proved by the iodine method that the constitution of the deposit dried under these conditions is only approximately represented by this formula.¹ Classen has shown that, if the peroxide be converted into the lower oxide (Mn_3O_4) by ignition, a compound of constant composition will be obtained, the weight of which multiplied

¹ *Zeitschr. f. angew. Chem.* 1895, 253.

by .720 will yield the weight of metallic manganese present in the electrolyte.

The electrolytic method for the determination of manganese, which until very recently suffered under the disadvantage that only very small amounts of manganese could be obtained as an adherent deposit of the peroxide, was naturally not fitted to compete with the gravimetric or volumetric processes for determining this metal.

The two electrolytic methods last described remove this disadvantage, it is true; but the volumetric process for manganese determination is so simple that one can hardly expect these improved electrolytic methods to replace it in technical laboratories.

SILVER

Silver is classed as one of the noble metals, and therefore one can prophesy that it will be possible to deposit it from solutions containing free acid. This prophecy is found to be correct; but the deposition of silver from such solutions is, from a practical point of view, attended by several objectionable features.

In the first place, silver, under certain conditions, separates concurrently as metal at the kathode and as peroxide at the anode. A further difficulty is caused by the character of the metallic deposit, which is compact, smooth, and bright only in exceptional cases, unless extremely feeble currents have been employed in electrolysing these acid solutions.

The neutral salts yield flocculent bulky deposits of a brown colour even with the feeblest currents and most dilute solutions. Luckow states that similar deposits are obtained from solutions to which ammonium hydrate and ammonium carbonate have been added, but in this case silver peroxide is deposited at the same time at the anode.

If free nitric acid be added to a solution of silver nitrate, the electrolysis of this mixture will yield, at times, adherent and bright deposits of the metal; but quite as

frequently greyish-brown non-adherent deposits will be obtained, with peroxide formation at the anode. The addition of lactic or tartaric acid prevents the peroxide separation.

Fresenius and Bergmann¹ have shown, however, that even with this addition it is only possible to obtain useful deposits from this solution with any degree of certainty, when using very feeble currents and a very dilute electrolyte.

On this account the time required to complete the separation of the metal is very great. In order to carry out such an electrolysis, a maximum of .50 grm. silver nitrate or silver sulphate is dissolved in water, and after addition of 5 to 6 c.cms. nitric acid the mixture is diluted to 125 or 150 c.cms., and is electrolysed at a temperature of 50° to 60° C. with a current density of .04 to .05 ampère. The separation will demand four to five hours.

The electrolysis with this solution may be carried out at the normal temperature, if a current density of from .10 to .20 ampère be not exceeded. The E.M.F. required in this case will be about 2 volts. Higher current densities than these, or insufficiency of nitric acid, cause the formation of peroxide and of non-adherent deposits of the metal.

The well-known reaction with chlorides is made use of to ascertain the completion of the electrolysis of the silver salt. The acid liquid must be washed out of the basin before breaking the circuit; the deposit of silver must be dried at 100° C. The colour of deposits of silver obtained from nitric acid solutions is white with a metallic lustre, and much resembles that of platinum when the electrolysis has been successfully carried out. Deposits that are a light greyish-brown in colour are untrustworthy.

The method proposed by Luckow,² in which the silver is deposited from the double cyanide salt of silver and potassium, is much to be preferred to that described above.

¹ *Zeitschr. f. anal. Chem.* **19**, 316.

² *Ibid.* 1.

The solution for this electrolysis is prepared by dissolving amounts not exceeding 1 gram. in weight of silver nitrate or silver sulphate in water, and by adding to this solution a freshly prepared solution of pure potassium cyanide until the precipitate of $\text{Ag}(\text{CN})_2$, which first formed, has dissolved in the excess of the potassium cyanide. Rather more than the exact amount necessary to obtain a clear solution is added. From 2 to 3 grms. solid potassium cyanide will be requisite. The solution is then diluted to 150 c.cms. It is advisable to make use of the purest potassium cyanide that can be obtained, since the use of the impure commercial product leads to a less satisfactory deposit of silver at the kathode. The current density employed with this solution may rise to 1 ampère without injury to the character of the deposit. If feeble currents of from .20 to .30 ampère be employed to effect the deposition at the normal temperature, the E.M.F. required will be between 3.3 and 3.5 volts, and the complete separation will demand four to five hours; if the currents be increased to .50 or .60 ampère, an E.M.F. of from 4.0 to 4.6 volts will be requisite, and the time will be reduced to from two to two and a half hours. The electrolysis may also be carried out with a heated electrolyte, without any danger to the character of the deposit.

Using a current density of 1 ampère and an E.M.F. of 5.8 volts, a solution containing .50 gram. of the silver salt heated to 60° C. will have all the silver deposited as a dead-white coating upon the kathode in half an hour. The E.M.F. required for such a heated solution when the current is reduced to .60 ampère is only 4.8 volts. This potassium cyanide method may also be used with extremely feeble currents—from .10 to .20 ampère—at the normal temperature, and on this account it may be employed for performing the electrolysis at night. The E.M.F. required in this case is 3.3 volts.

The deposit obtained from the double cyanide solution is of a dead silver-white colour, and therefore differs in this respect from that obtained from the acid solutions.

The deposit appears to be partly crystalline in structure, but in spite of this it adheres firmly to the electrode. The use of roughened or well-used electrodes as kathodes is found to be advantageous. The dead-white appearance of the deposit is at times found to give place to patches of brown. This indicates that at these spots the current density has been too great, a result that can easily arise with certain forms of electrodes. When a basin electrode has been employed, the liquid must be washed out before breaking the circuit. This and the remaining washing and drying operations are carried out exactly as described for copper and the other metals of this group.

Krutwig has recommended an ammoniacal solution of silver containing ammonium sulphate, for obtaining deposits of this metal.¹ In order to prepare such a solution .50 grm. silver nitrate or silver sulphate is dissolved in water, and to this solution 25 c.cms. ammonium hydrate and a solution of 6 grms. ammonium sulphate are added. This mixture is heated, and, according to v. Miller and Kiliani,² should be electrolysed with a current density of from .02 to .05 ampère. The E.M.F. required will be about 2.5 volts. The results obtained by use of this method are uncertain. Stronger current densities result always in the separation of the silver in a loose flocculent form, greyish brown in colour, at the kathode, a result which cannot be avoided by lessening the amount of ammonium hydrate. The deposit of metal also encloses ammonium sulphate, and for the removal of this a very careful washing with water is required. The method therefore cannot be recommended.

Other proposals emanate from Brand and from Smith. The former has suggested the use of an ammoniacal sodium pyrophosphate solution,³ the latter the use of an ammoniacal phosphate solution.⁴ Neither of these methods yields satisfactory results.

Luckow has shown that in the case of silver it is

¹ *Berichte*, 15, 1267.

³ *Berichte*, 28, 581.

² *Lehrbuch der Analyse*.

⁴ *Amer. Chem. Jour.* 1890, 12, 329.

possible to directly decompose insoluble salts—such as the chloride, bromide, and iodide—by electrolysis, if these are first covered with dilute acetic or sulphuric acid.¹ In order to effect this decomposition, the finely ground insoluble salt is placed at the bottom of a beaker in which a cone electrode functions as kathode. On making the necessary current connections, it will be found that the powder gradually disappears from the bottom of the vessel. If the basin electrode be used, this must be connected to act as anode; the deposit of silver will then be found upon the smaller disc. If strong currents be used, similar objectionable features will occur in relation to the deposition of the silver as those noted in the case of the nitric acid solution. It may therefore be regarded as more advantageous to bring the insoluble halogen salt of silver into solution by aid of potassium cyanide, and then to decompose this double cyanide solution in the way already described.

From the statements concerning the usefulness of the different methods that have already been made in the descriptions of them, it will have been gathered that only one method fulfils the requirements demanded in a satisfactory and reliable process for the electrolytic separation of silver—namely, the potassium cyanide method.

Since in technical work it is extremely rarely that pure solutions of silver are at one's disposal for analysis, it is not at all probable that the electrolytic method will displace the usual gravimetric or volumetric processes of analysis.

MERCURY

This metal, which differs from all others in its property of being fluid at the normal temperature, electrolytically considered, exhibits likewise distinctive characteristics. The separation of mercury occurs in the form of tiny spherical globules, which nevertheless adhere comparatively firmly to the electrode surface.

¹ *Zeitschr. f. anal. Chem.* 19, 1.

These tiny spheres of the metal increase in size, and ultimately run together to form small drops, when larger amounts of mercury are deposited.

In the case of some of the solutions used for effecting mercury depositions, the first form of the deposit lasts for a longer period than in the case of other solutions, as, for example, acid solutions ; and it is therefore possible with these solutions to separate a larger amount of mercury as a uniform coating of the metal upon the electrode.

A spongy formation of the deposit is, in the case of this metal, perfectly impossible ; and it therefore follows that most solutions of mercury yield, on electrolysis, deposits which are perfectly satisfactory in character.

On account, however, of the tendency of the fluid metal to collect into drops upon the bottom of the basin in which the electrolysis is conducted, there is a practical limit to the amount of mercury which may be separated. This limit is about 2 grms. metal ; above this, the washing and drying of the deposits is difficult or impossible. The jacket electrodes are not so well adapted for this electrolysis as the basin electrode. When the deposition is completed the electrolyte is washed out before breaking the circuit, the deposit upon the basin is washed several times with water, and, the alcohol wash being omitted, it is finally dried in the desiccator over sulphuric acid. If the metal should have collected into larger drops, and so have rendered it difficult to pour away the wash-water without loss of mercury, it will be found most easy and safe to remove the remaining portions of the wash-water by means of filter paper.

In the case of mercury the use of alcohol must be avoided, since it produces a grey dull skin upon the surface of the metal.

A basin having a roughened or at least dulled inner surface is recommended for this electrolysis.

Luckow¹ and Smith and Knerr² state that the neutral

¹ *Zeitschr. f. anal. Chem.* 19, 1.

² *Amer. Chem. Jour.* 8, 206.

salts—the chlorides, sulphates, and nitrates—in either the mercurous or mercuric form, permit complete separation of the metal ; but these neutral solutions are such bad conductors that it is more advantageous to add to them 1 or 2 per cent. sulphuric or nitric acid, as recommended by Clarke,¹ Rüdorff,² Classen and Ludwig,³ and Smith and Moyer.⁴ In order to prepare such a solution .50 gm. mercuric chloride is dissolved in water, 1 to 2 c.cms. sulphuric acid are added, and the mixture is then diluted to the usual volume. This is now electrolysed at the normal temperature with a current of from .60 to 1.0 ampère. The E.M.F. required will vary from 3.5 to 5.0 volts, according to the amount of acid present. The separation will be complete in two to two and a half hours. The metal will be found in tiny bright and silvery spherical globules, which, if the quantities named above have been used, will adhere firmly to the walls of the basin, although here and there they may have run somewhat together to form larger spheres. In order to test whether the electrolysis of the mercury salt is complete, sulphuretted hydrogen gas is passed through the small test-portion of the electrolyte, or a few drops of ammonium sulphide are added to the same. The presence of mercury is marked by a brownish tint in the mixture. The washing and drying of the mercury is carried out as already described.

Similar results are obtained when nitric acid is used in place of sulphuric acid. In this case the solution is prepared by adding 3 c.cms. nitric acid to .50 gm. mercuric chloride dissolved in water, and by diluting the mixture to 150 c.cms. This solution may be electrolysed with a current density of 1 ampère at the normal temperature.

An E.M.F. of 3.6 to 4.0 volts will be required ; the time will be between two and a half and three hours. The character of the deposit resembles that obtained with sulphuric acid.

¹ *Amer. Jour. of Sc. and Art*, 16, 200.

² *Zeitschr. f. angew. Chem.* 1894, 388.

³ *Berichte*, 19, 324.

⁴ *Jour. Anal. and Appl. Chem.* 1893, 7, 252.

Classen¹ and de la Escosura² have pointed out that similar results can be obtained by use of a mercuric chloride solution containing hydrochloric acid or sodium chloride. This solution, however, on electrolysis produces chlorine, and therefore its employment cannot be recommended.

It was noted under Silver that the deposits obtained from the cyanide solution were dead white, as opposed to the metallic lustre of those obtained from the acid solutions. Smith and Frankel,³ Smith and Cauley,⁴ and Smith and Wallace⁵ have noted that mercury behaves in a similar manner. If .50 grm. mercuric chloride be dissolved in water, and 3 grm. pure potassium cyanide be added, a clear solution will be formed. This may be diluted to 150 c.cms. and electrolysed at the normal temperature with a current density of from .50 to 1.0 ampère. The deposit of mercury obtained will closely resemble the dead-white silver deposit described under Silver, and only few of the tiny globules of the metal which compose it will run together.

The E.M.F. required will be between 5.5 and 6.0 volts, and about an hour will suffice to deposit the whole of the mercury. The results are equally satisfactory when the electrolysis is performed at the normal temperature with a current density of only .02 ampère ; in this case the complete separation of the metal from the solution demands twelve hours. The cyanide solution may also be heated to 60° C. without any injury to the character of the deposits, and under these conditions the separation will be completed in a shorter time than any mentioned above.

Mercury is often present as the sulphide in solutions obtained in the course of analysis, and it is therefore of some convenience that this metal can be quantitatively separated by electrolysis from a sodium sulphide solution.

¹ *Electrolyse* (Text-book).

² *Revista Minera*, 1886 (Madrid).

³ *Jour. Franklin Inst.* 127, 469.

⁴ *Jour. Anal. and Appl. Chem.* 1891, 5, 489.

⁵ *Berichte*, 1892, 779.

This method has been described by de la Escosura, Smith,¹ and Vortmann.²

In order to carry out such a determination, 50 grm. mercuric chloride is dissolved in water, and sulphuretted hydrogen gas is passed through the solution until all the mercury is precipitated. From 40 to 50 c.cms. of a saturated solution of sodium sulphide and a small portion of sodium hydrate are now added, and the clear solution which is thus obtained is diluted to 150 c.cms. At the normal temperature an E.M.F. of 3.5 to 4.0 volts is required to produce a current density of 1 ampère: if heated to 50° to 60° C. an E.M.F. of 3 volts suffices for this; in either case the separation of the mercury occurs satisfactorily, and the time required is about an hour. If a sufficiency of sodium sulphide has been used, sulphur will separate at the anode; if the reverse has been the case, a dark-coloured deposit of mercuric sulphide mixed with sulphur will be obtained there. Similar deposits are obtained with antimony and tin, of which further mention will be made later. The amount of sodium sulphide named above is ample to hinder this result. In order to judge when the separation is completed, the small test-sample of the electrolyte is treated with a few drops of acid. A brown coloration of the liquid indicates the presence of mercury. The reaction with sulphuretted hydrogen cannot be employed in the case of the above solution. The character of the deposit of mercury at the kathode closely resembles that of the deposit obtained from the nitric acid solution.

In addition to the solutions that have already received notice, Schmucker has recommended solutions containing ammonium tartrate,³ whilst Vortmann⁴ and Classen⁵ have recommended the addition of ammonium oxalate. The use of the former solution is attended by the usual disadvantages

¹ *Jour. Anal. and Appl. Chem.* 1891, 5, 202.

² *Chem. Zeitg.* 1881, 390.

³ *Zeitschr. f. anorg. Chem.* 5, 206.

⁴ *Berichte*, 24, 2750.

⁵ *Zeitschr. f. Elektrochem.* 1894, 1, 280.

of the tartrate methods ; the latter gives useful results. A solution containing .50 grm. mercuric chloride is mixed with one containing between 4 and 5 grms. ammonium oxalate, and after dilution to 150 c.cms. the mixture is electrolysed at the normal temperature with a current density of 1 ampère. The E.M.F. required will be between 4 and 4.6 volts ; the time from one and a half to two hours.

Solutions containing sodium pyrophosphate and ammonium hydrate or ammonium carbonate only yield satisfactory results with the mercuric salts. With a current of .20 ampère the deposition occupies five hours.

Insoluble compounds of mercury may be directly decomposed by the electrolytic method, as in the case of the similar compounds of silver. An indication of the possibility of this is given in the observation that may be made in the course of some of the preceding experiments. In the case of many solutions of mercuric chloride, this latter is converted by the action of the current into insoluble mercurous chloride, before it is completely decomposed. The cloudy appearance of the electrolyte—due to mercurous chloride—disappears again after some interval of time. The procedure is very similar when mercurous chloride is placed upon the bottom of a beaker, covered with water containing hydrochloric acid or sodium chloride, and electrolysed. Other mercury compounds which may be decomposed in this way are mercuric sulphide and cinnabar. This method has in fact been in use for a considerable time at the mines in Almada, in Spain, for determining the percentage of mercury in pieces of pure cinnabar. It is only possible, however, to use very feeble currents to effect the separation, and on this account the electrolysis requires twelve to eighteen hours ; this is too long a period for practical purposes.

In order to effect the removal of the deposited mercury from the basin or from the conical electrode, nitric acid is used ; and the solution is hastened by heating. It frequently occurs, however, that round the top edge of the

deposit a dark-coloured band, insoluble in nitric acid, remains upon the platinum. In these cases one may either attempt to remove it by raising the basin to a red heat, or by using the basin as anode with an electrolyte containing nitric acid, and a stout copper wire as kathode. This deposit can be removed by either of these methods, in most cases very quickly.

It is noteworthy that the electrodes lose slightly in weight with every successive mercury determination ; on this account it is necessary to reweigh them after each electrolysis of a mercury solution.

Since nearly all the methods described for the electrolytic determination of mercury yield equally good deposits on the kathode, it follows that the selection of the best method rests upon the time required for the deposition. The nature of the solution, or the form in which the mercury is obtained in the ordinary course of the analysis, must, however, be permitted to exert some influence upon the selection of the method. If the mercury is obtained in an acid solution, it is of course most convenient to use this directly for the deposition ; if mercuric sulphide is obtained, the method with sodium sulphide is used. For solutions of the neutral salts in the case of which any one of the described methods is directly applicable, the potassium cyanide method is to be preferred.

The electrolytic method for mercury determinations can be advantageously used in the case of pure salts or their solutions. It is not equally well suited for determining the amount of the metal in the ores of mercury, because, as will be pointed out later, the separation from several of the other metals is difficult, or for technical purposes inconvenient.

ANTIMONY

This metal exhibits electrolytic characteristics which differ somewhat from those of any of the metals that have hitherto been considered. Its position in the list of metals

given earlier would lead one to suppose that antimony can be deposited from acid solutions ; this supposition is found to be correct. Classen and V. Reiss (*l.c.*) have shown that this metal may be deposited from solutions containing hydrochloric acid ; while Gore and Sanderson have noted that solutions containing ammonium or sodium chloride are equally serviceable.¹ The deposits obtained in this way are, however, not sufficiently adherent to the electrode to be regarded as satisfactory ; and that obtained from the hydrochloric acid solution is further unfitted for analytical purposes on account of its explosive properties. Gore, and Classen and V. Reiss, have recommended solutions containing oxalates of the alkali metals, but these yield metallic deposits which are still less adherent than those obtained from the first-named solutions.

The addition of ammonium pyrophosphate produces no better results.

The electrolysis of a solution of antimonyl potassium tartrate (tartar emetic), or of an antimony solution containing tartaric acid, yields a deposit which is entirely satisfactory ; the electrical resistances of these solutions are however so great (as with all other solutions containing chiefly tartrates) that the separation takes place too slowly for practical use.

The sulpho-salt of antimony, as proposed by Parrodi and Mascazzini,² Luckow,³ Classen and V. Reiss,⁴ Classen,⁵ and Classen and Ludwig,⁶ is the best to use for obtaining satisfactory antimony deposits. It is necessary to prepare a saturated solution of sodium sulphide from the pure crystallised salt, for use in this method. This solution requires filtering before employment. A solution of 1 grm. tartar emetic, in water, is treated with this sodium sulphide solution until the precipitate which first forms is

¹ *Berichte*, Ref. 1891, 340.

² *Gazz. chim. Ital.* 8, 1879 ; *Zeitschr. f. anal. Chem.* 18, 588.

³ *Zeitschr. f. anal. Chem.* 1880, 19, 1.

⁴ *Berichte*, 1881, 14.

⁵ *Ibid.* 1884, 17, 2476.

Ibid. 1885, 18, 1104.

redissolved. The mixture, after dilution to 150 c.cms., is electrolysed at the normal temperature with a current density of from .50 to 1.0 ampère.

The E.M.F. required will be between 1.3 and 1.8 volts ; the separation will demand from six to seven hours. It is more advantageous to heat the electrolyte to 70° or 80° C., and to use a current density of between 1.0 and 1.5 ampères. The E.M.F. required under these conditions will lie between 2.5 and 3.2 volts ; the time will be only one and a half hours. In order to test whether any antimony still remains in the electrolyte, the small test portion of the latter is heated with a few drops of dilute sulphuric acid. If antimony be present, the sulphur which separates owing to decomposition of some of the sodium sulphide will be reddish in colour, by reason of the admixture of antimony sulphide.

One may also use the method of testing for the end of the electrolysis, described fully under 'Copper,' dependent upon raising the level of the electrolyte in the basin or beaker by addition of water. This method is, however, not very trustworthy, if the amount of remaining metal be small. When the electrolysis is completed, the electrolyte is washed out of the basin before breaking the circuit, and the washing and drying of the deposit are carried out as usual. The deposit of antimony obtained from these sulphide solutions is bright, metallic, and silver grey in colour ; and if a well-worn electrode has been used as the kathode, it is extremely adherent to the platinum surface.

It is therefore advisable, if such an electrode be not at hand, to artificially roughen one by means of a sand blast, before carrying out electrolytic determinations of this metal. While a deposit of metallic antimony of the character just described is obtained at the kathode, the anode becomes coated with a yellowish white deposit of sulphur, which may easily be removed by rubbing. Equally good results are obtained, when any other salt of antimony than that known as tartar emetic is converted into the sulpho-salt by means of sodium sulphide.

The special advantage of this method—apart from the easy separation of antimony from other metals which it affords—lies in the fact that the form in which the metal is submitted to electrolysis is that in which it is obtained, in the customary course of analysis. It must, however, be noted that the substitution of potassium sulphide for sodium sulphide is not feasible ; from such a solution complete separation of the antimony does not occur.

If the sodium sulphide solution used in preparing the electrolyte should contain polysulphides, the presence of which is indicated by its dark yellow colour, the separation of the antimony will not be quantitative, and may even be checked very early in the electrolysis. It is therefore best to use a solution containing only the monosulphide ; and one containing free alkali is to be preferred to one holding too much sulphur. Polysulphides are, however, produced in the electrolyte during the course of the electrolysis, and

the current be allowed to continue for too lengthy a period of time, the edges of the deposit may be dissolved ; and this redissolved antimony cannot then be separated from the electrolyte. The deposition of antimony from a sodium sulphide solution can be carried out at the normal temperature during the night by means of a current density of $\cdot 30$ to $\cdot 40$ ampère ; the E.M.F. required will be between $1\cdot 7$ and $1\cdot 8$ volts, and the time for complete separation about twelve or fourteen hours.

It is however preferable to carry out the electrolysis with hot solutions and strong currents in a short time, since the above-named difficulty caused by re-solution of the deposit is often found to occur when the current is left in operation over night. If the solution obtained for electrolysis should contain polysulphides, these must be decomposed by means of hydrogen peroxide, and a fresh amount of sodium monosulphide must then be added to the solution.

The removal of the deposit of antimony from the platinum electrode is effected by means of hot nitric acid.

A white oxide of antimony is formed, which passes into solution, if tartaric acid be added to the nitric acid; or this oxide may be removed by simply rinsing out with water or by rubbing the electrode with a cloth. If a greyish discoloration should remain at its edges, this may be removed by treatment with dilute hydrochloric acid.

The determination of antimony by the electrolysis of its sulpho-salt is one of the most convenient and useful of all electrolytic methods, and is one that is frequently used in actual practice. It is especially convenient, because the form of solution in which the antimony is obtained in the usual course of separation from the other metals can be directly electrolysed. Further, this method affords a simple means for separating antimony from tin and arsenic—a separation that by the usual methods of analysis is difficult to effect. This will, however, receive fuller notice later.

ARSENIC

This metal cannot be quantitatively separated by means of electrolytic methods of analysis. From solutions containing hydrochloric acid no deposition occurs, since the arsenic combines with the hydrogen at the surface of the kathode and forms arseniuretted hydrogen, which escapes as a gas. Solutions to which oxalates and similar salts have been added give incomplete deposits on electrolysis; while even the sulpho-salt solutions fail to give satisfactory results according to Luckow,¹ Classen and V. Reiss,² and Moore.³ Vortmann has described attempts to separate the arsenic as an amalgam with mercury;⁴ the results were unsuccessful, owing to incomplete separation of the arsenic.

TIN

Tin in its electrolytic characteristics closely resembles antimony. Solutions of stannous and stannic chloride may

¹ *Zeitschr. f. anal. Chem.* **19**, 1.

² *Chem. News*, **53**, 209.

³ *Berichte*, **14**, 1622.

⁴ *Berichte*, **24**, 2750.

be decomposed by the current, and yield a deposit of metallic tin. Other solutions of tin containing free hydrochloric acid give similar results. The deposit inclines to a coarse crystalline structure ; and both on this account, and on account of the disagreeable features of the electrolysis of chloride solutions, except when absolutely necessary this method is little used.

Tin, like zinc, forms with excess of sodium hydrate a complex salt—sodium stannate.

If a tin solution containing such an excess of sodium hydrate be submitted to electrolysis, either heated or at the normal temperature, with a current of from .50 to 1.0 ampère, a separation of spongy tin will result ; and only a very small amount will be obtained as a metallic deposit of a silver white colour. The E.M.F. required will be from 4.0 to 4.5 volts. The greyish spongy deposit of tin is not composed of loose flaky particles, as in the case of the other metals, but consists of a network of numberless tiny shining needles. Solutions containing, in addition to the caustic hydrate, potassium cyanide, yield deposits of a similar character under the above conditions of current, E.M.F., and temperature.

Classen and V. Reiss (*l.c.*) have proposed the use of the double oxalate of tin and ammonium. This solution yields a metallic deposit ; but when neutral, white particles of stannic oxide separate during the electrolysis ; and an addition of oxalic acid is necessary to bring these again into solution. In these cases, therefore, in which this method is to be used it is more advantageous to employ the acid oxalate of ammonium, or to add to the neutral double oxalate solution, oxalic or acetic acid. In order to prepare such a solution for electrolysis, .50 gm. stannous chloride is dissolved with the aid of a little hydrochloric acid, the excess of acid is neutralised with ammonium hydrate, and a solution of 4 grms. ammonium oxalate is added. The precipitate which at first forms redissolves. The mixture is then acidified with oxalic acid ; or an equal weight

of the acid oxalate of ammonium might have been used, in place of the 4 grms. of the neutral salt. With a current of from .30 to .40 ampère in density at the normal temperature the separation requires an E.M.F. of from 2.8 to 3.5 volts, and lasts from six to seven hours. The neutral double salt solution may also receive an addition of 10 c.cms. acetic acid, and be electrolysed with a current of .50 ampère at the normal temperature. In this case the E.M.F. required is between 3.3 and 3.8 volts, and the separation demands from five to six hours. Towards the end of the deposition an increase of the current strength is necessary, in order to effect the separation of the last traces of the metal from the electrolyte. The deposits obtained from these solutions are adherent, silvery, white, and metallic ; they are washed and dried in the customary manner.

Since tin is frequently obtained in the usual course of analysis as stannic or stannous sulphide, it is a great advantage that tin can be quantitatively separated from solutions of the sulpho-salt. A complete separation is, however, only possible when using the ammonium salt solution ; the deposition is incomplete when the potassium or sodium salt is used. In order to prepare the solution of ammonium sulphide, sulphuretted hydrogen is passed through ammonium hydrate until no more of this gas is absorbed ; and in order to produce polysulphides (in the case of antimony these had to be avoided) some powdered sulphur is added. A solution of .50 gm. stannous chloride in water containing a little hydrochloric acid is now prepared, the tin is precipitated by sulphuretted hydrogen, and the well-washed precipitate is dissolved in from 10 to 15 c.cms. of the above ammonium sulphide solution.

After dilution to 150 c.cms. the solution is electrolysed either at the normal temperature, with a current of between .50 and .70 ampère in density, or better, at a temperature of 50° to 60° C., with a current of from 1.0 to 2.0 ampères. In the latter case an E.M.F. of between 3.3 and 4.0 volts will be required, and the time occupied in the separation will be

only one hour, as compared with the five or six hours demanded in the former case. The deposits obtained in this way are bright steel grey. The end of the electrolysis is checked by treating the small test portion of the electrolyte with a few drops of dilute sulphuric acid and by gently heating the mixture. If the turbidity which is produced owing to the decomposition of the ammonium sulphide remains white no tin is present ; if it changes to a greyish-brown tint, the whole of the metal has not been deposited. When the deposition of the tin is completed the remainder of the electrolyte must be washed from the basin before the circuit is broken. In order to effect the removal of the deposit from the electrode, it may be warmed with concentrated hydrochloric acid.

Engels has recently shown that a clear solution of a tin salt to which a little hydroxylamine and sulphuric acid have been added, can be prepared for electrolysis in such a way that no separation of stannic oxide will occur during the deposition of the tin, and that the character of the deposit obtained at the kathode, even under the most divergent conditions of current and temperature, will be all that can be desired. If on solution of the salt in water a slight turbidity is produced, this is removed by the addition of a little oxalic acid. This solution—which should contain an amount of the salt = $\cdot 30$ grm. tin—then receives an addition of $\cdot 30$ to $\cdot 50$ grm. hydroxylammonium sulphate or chloride, 2 grms. tartaric acid, and 2 grms. ammonium acetate, and after dilution to 150 c.cms. it is electrolysed at a temperature of 60° to 70° C., with a current density of from $\cdot 70$ to $1\cdot 0$ ampère. The E.M.F. required will lie between 4.2 and 5.6 volts, and the time demanded for the complete separation of the tin as a silver-white metallic deposit will be three to three and a half hours.

In consequence of the difficulties that arise when commercial stannous chloride is dissolved in water, and in order to avoid the unpleasantness of manipulating stannic chloride, it is advantageous to prepare the double salts of

tin with ammonium or the alkali metal chlorides, for electrolytic experiments.

The stannous and stannic salts of this type are all soluble in water.

Of the methods described above, only one—the sulpho-salt method—is actually used in technical laboratories. As a general rule, tin is obtained in the ordinary course of analysis either in the form of oxide—when it is more simple to ignite and to weigh this, than to bring into solution for electrolysis—or as stannous or stannic sulphide. In the latter case, the electrolytic method with ammonium sulphide is useful. This latter method is also of technical importance in the separation of antimony, arsenic, and tin.

GOLD

Gold, being one of the noble metals, may be deposited from acid solutions.

Solutions containing free hydrochloric acid may be used, or even neutral solutions of gold chloride. Luckow¹ and Brugnatelli² have shown that the double salts with sodium or ammonium chlorides may also be used. The deposits of gold obtained from these solutions are unfortunately powdery in nature, and brown in colour, even when currents of moderate intensity are used.

The solution of gold with excess of potassium cyanide, recommended by Elkington, Ruolz, de la Rive, Luckow, and Smith and Moore,³ is that chiefly used for obtaining deposits of this metal; and in this respect gold shows its kinship to silver. In order to carry out such an electrolysis a solution of gold chloride, containing about .10 gm. gold, receives an addition of 1.5 gm. potassium cyanide; and after dilution to the usual volume the mixture is electrolysed with a current density of .10 ampère. The deposition will be complete in from ten to twelve hours.

¹ *Zeitschr. f. anal. Chem.* 19, 14. ² *Phil. Magazine*, 21, 187.

³ *Berichte*, 1891, 2175.

The deposit of gold adheres firmly to the platinum of the electrode, and, if one would avoid attacking the latter when dissolving off the coating of gold by means of aqua regia, it is necessary, as in the case of zinc, to protect the electrode with a coating of silver or of copper.

If for any reason it may be desired to dispense with this coating, the gold deposit may be removed from the electrode by covering it with a dilute potassium cyanide solution, and by electrolysis with a stout copper wire as kathode, and the platinum electrode with its coating of gold as anode.

Gold resembles antimony and tin in its property of forming soluble double salts with the alkali-metal sulphides, the solutions of which on electrolysis yield useful deposits. The sodium double salt is exceptionally suited for this use; while Smith and Wallace¹ have shown that the double ammonium sulphide does not yield quantitative results. In order to prepare such a solution, sodium sulphide solution (saturated) is added to a solution of gold chloride until the precipitate which first forms is re-dissolved. This solution is diluted to about 125 c.cms., and on electrolysis by means of currents of from .10 to .20 ampère at the normal temperature, an adherent deposit of a brilliant yellow colour is obtained.

Smith has shown that useful deposits may likewise be obtained from gold solutions containing 5 c.cms. free phosphoric acid,² by means of current densities of .08 to .10 ampère; and Bersoz proved so long ago as 1847 that similar results could be obtained by use of gold solutions containing sodium pyrophosphate.³

Only the methods with potassium cyanide, and that depending upon the formation of the sulpho-salts, are used in practical work. For gold determinations by the electrolytic method it is advisable always to choose the smaller and

¹ *Proc. Chem. Soc. Frankl.* 3, 20.

² *Amer. Chem. Jour.* 1891, 13, 206.

³ *Anal. Chem. Pharm.* 1847, 65, 164.

lighter electrode as kathode, since as a rule the amount of gold obtained is very small.

On account of the difficulty of separating gold from the other metals by electrolysis, no displacement in technical laboratories of the usual dry assay methods by the introduction of the electrolytic methods described above is likely to occur.

PLATINUM

This metal, which likewise belongs to the group of the noble metals, may be deposited from solutions containing free hydrochloric or sulphuric acid. If the current used be not extremely feeble (under $\cdot 10$ ampère) the metal will be obtained as a black loosely adherent powder at the kathode, instead of as a bright and dense metallic deposit.

In this case, as in that of gold, it is preferable to protect the electrode surface with a coating of silver or copper. A solution of platinum chloride, or of the double chloride of potassium and platinum, to which a few drops of concentrated sulphuric acid have been added, is recommended by Classen and Halberstadt,¹ Rüdorff,² and V. Miller and Kiliani³ for obtaining deposits of this metal. An E.M.F. of 2 volts (that given by a single accumulator cell) suffices to carry out this electrolysis. The solution is heated and is electrolysed with current densities of between $\cdot 01$ and $\cdot 03$ ampère.

An E.M.F. of from 1.1 to 1.7 volts will be required; and the time necessary to deposit $\cdot 20$ to $\cdot 30$ gm. platinum will be from four to five hours. The only test which can be applied in order to determine the end of the electrolysis is that depending upon the addition of water to the solution and consequent raising of level of the electrolyte.

Smith has proposed the use of solutions containing

¹ *Berichte*, 17, 2477. ² *Zeitschr. f. angew. Chem.* 1892, 696.

³ *Lehrbuch der Analyse*.

sodium phosphate and free phosphoric acid for obtaining deposits of platinum.¹ A current of .07 ampère must be used ; and ten hours are requisite to effect the separation of .10 grm. metal.

Classen and Halberstadt (*l.c.*) have experimented with platinum solutions containing potassium or ammonium oxalate ; while Wahl has made attempts to obtain useful deposits of the metal from solutions containing only oxalic acid in addition to the platinum salt.²

The double salt of platinum with potassium cyanide has also been used with success, for obtaining deposits of this metal.

The electrolytic determination of platinum is of no practical importance.

PALLADIUM

Schucht has shown that palladium is separated concurrently as metal and as oxide from solutions containing free nitric acid, and also from those containing excess of sodium hydrate.³ When, however, the solutions corresponding to those given above for platinum are employed, the metal alone is obtained. If the currents be feeble, dense metallic deposits are obtained ; if strong currents be used, the metal separates at the kathode as a black powdery mass. Joly and Leidié electrolysed a solution of the double chloride of potassium and palladium when engaged upon an atomic weight determination.⁴

Smith and Keller have shown that palladium may also be deposited from ammoniacal solutions.⁵

In order to obtain a palladium deposit from such a solution, the chloride is dissolved in water, and is treated with ammonium hydrate and hydrochloric acid, and finally

¹ *Amer. Chem. Jour.* 1891, 13, 206.

² *Jour. Frankl. Inst.* 132, 62.

³ *Berg. u. Hüttenzeitg.* 1880, 39, 121.

⁴ *Compt. Rend.* 116, 146.

⁵ *Amer. Chem. Jour.* 1890, 12, 252.

20 c.cms. ammonium hydrate are added in excess. After dilution to the usual volume, this mixture is electrolysed with a current of from .07 to .10 ampère. If the electrolysis be allowed to continue through the night, .20 to .30 gramm. palladium can be separated in this way.

The remark made concerning the practical importance of the electrolytic methods for determining platinum applies in this case also.

IRIDIUM

There is but little known concerning the deposition of this metal from its solutions by means of the electric current. Schucht states that it may be separated in adherent and bright metallic form from solutions acidified with dilute sulphuric acid.¹

From solutions containing sodium phosphate and free phosphoric acid, on the other hand, no deposition is obtained, and Smith has suggested the use of this solution in order to effect the separation of iridium from platinum and palladium.²

RHODIUM

There is little more known concerning the electrolytic separation of this metal than in the case of iridium. Joly and Leidié have shown that the metal is separable from solutions slightly acidified with sulphuric acid.³ The solution of the sesquichloride to which alkali metal chlorides and hydrochloric acid have been added may also be decomposed by the current with separation of the metal. Smith states that a complete deposition of the metal is obtained when a solution of the double chloride of rhodium and sodium to which sodium phosphate and phosphoric acid have been added is electrolysed.⁴

¹ *Berg. u. Hüttenzeitg.* 1880, 39, 122.

² *Amer. Chem. Jour.* 1892, 14, 435.

³ *Compt. Rend.* 1891, 112, 793.

⁴ *Amer. Chem. Jour.* 1892, 14, 435.

THALLIUM

This metal in many of its electrolytic characteristics resembles lead. It possesses the property of separating from certain solutions both as metal and as oxide. It is quite possible so to conduct the electrolysis with other solutions that only the metal separates at the kathode ; but this metallic deposit is so easily oxidised that it is not fitted for quantitative determinations. Schucht has shown that under certain conditions it is possible to obtain a deposition of pure thallium peroxide (similar to that of lead) from solutions containing free nitric acid.¹ This method, however, cannot be used for quantitative purposes, as the separation occurs on both electrodes. The same result is found to occur if an alkaline or ammoniacal solution be used ; while from neutral solutions and from solutions containing sulphuric acid the deposition is incomplete. The solutions prepared with an excess of potassium cyanide and ammonium oxalate—i.e. solutions of the double cyanides and the double oxalates—yield with currents of .10 ampère the whole of the thallium as metal at the kathode, but these deposits cannot be washed or dried without the occurrence of oxidation. Neumann has shown that in such cases the determination of the weight of metal can be effected by placing the electrode with its metallic deposit in a suitable apparatus and adding hydrochloric acid ; the volume of hydrogen liberated is quantitatively proportional to the weight of metal dissolved.² The electrolytic determination of thallium is therefore always somewhat inconvenient and lengthy.

BISMUTH

Bismuth likewise belongs to that group of metals which separate on electrolysis of their solutions, concurrently as metal and oxide. Schucht has shown that the electrolysis

¹ *Berg. u. Hüttenzeitg.* 1880, 39, 121.

² *Berichte*, 21, 356.

of the neutral salt solutions yields metal at the kathode and yellow bismuthic acid at the anode.¹ It is not possible so to carry out this electrolysis that no metal is deposited ; but it may be conducted so that no peroxide is formed. It is, however, only in exceptional instances that the metal is obtained, even in small amounts, as a silvery white and metallic deposit ; as a rule the deposited metal is not only dark in colour, but is a powdery deposit of spongy formation, and is only loosely adherent to the electrode.

It is true that results have been obtained in very carefully conducted analyses, which, in spite of the unsuitable character of the deposit, have closely agreed with those obtained by other methods of analysis. The results obtained, however, with these deposits of a powdery character must always be regarded with distrust.

According to Smith and Knerr,² and Thomas and Smith,³ a solution of bismuth sulphate containing .15 gm. bismuth, to which 3 c.cms. dilute sulphuric acid have been added, if diluted to 150 c.cms. and electrolysed with a current of .30 ampère, gives in about three hours a fairly adherent deposit, which may be washed with care without loss.

Wieland also states that an adherent deposit may be obtained from solutions containing 5 c.cms. free nitric acid if the current density be kept below .05 ampère.⁴ According to Smith and Saltar, on the other hand, the nitric acid used ought not to be greater in amount than is necessary to effect the solution of the basic salt.⁵ If a greater amount than this be used, oxygen products of bismuth will separate at the anode.

The end of the electrolysis must be determined by treating the test-sample of the electrolyte with sulphuretted hydrogen.

¹ *Berg. u. Hüttenzeitg.* 1880, 39, 121.

² *Amer. Chem. Jour.* 1886, 8, 206.

³ *Ibid.* 1883, 5, 114.

⁴ *Berichte*, 17, 1612.

⁵ *Zeitsehr. f. anorg. Chem.* 1893, 3, 416.

Classen and V. Reiss,¹ Classen and Eliasberg,² and Vortmann³ have also made experiments bearing upon the use of the double oxalate salts of bismuth with ammonium or potassium, for electrolytic separations.

This method suffers under two disadvantages—in the first place, bismuth oxalate is only slightly soluble in ammonium oxalate; and, secondly, oxygen compounds separate at the anode as before. The method proposed by Brand (*l.c.*), in which sodium pyrophosphate and ammonium hydrate are used, also yields unsatisfactory results; and that proposed by Rüdorff, in which the bismuth solution is treated with quite a selection of chemicals—potassium oxalate, potassium sulphate, and sodium pyrophosphate—is similarly useless.

Other proposals are the addition of citric acid to either acid or alkaline bismuth solutions, by Thomas and Smith, Schmucker,⁴ and Smith and Frankel,⁵ and the addition of tartaric acid to alkaline or ammoniacal solutions.

None of these methods give really satisfactory results. On this account, when it is desired to effect the electrolytic determination of bismuth it is necessary to make use of the fact that bismuth combines with mercury to form an amalgam, and to deposit these two metals together. This method will receive further notice under the heading 'Amalgams.'

URANIUM, MOLYBDENUM, MAGNESIUM, ALUMINIUM, CHROMIUM, CALCIUM, BARIUM, STRONTIUM, POTASSIUM, SODIUM

Uranium and molybdenum can only be electrolytically separated from their solutions in the form of oxides, and the separation of these is frequently incomplete.

Magnesium, aluminium, and chromium can never be

¹ *Berichte*, 14, 1620.

² *Ibid.* 19, 326.

³ *Ibid.* 24, 2750.

⁴ *Zeitschr. f. anorg. Chem.* 5, 199.

⁵ *Amer. Chem. Jour.* 12, 428.

separated as metals from solutions of their salts in water under the customary conditions as regards concentration and current of electrolytic analyses. In some cases the separation of the hydroxide occurs.

The alkali metals, under similar conditions, are also incapable of depositions.

The alkaline earth metals, when present in hydrochloric or nitric acid solutions, are not deposited ; if, however, organic acids be present in the solution, the decomposition of these leads to the formation of carbonates or hydroxides, which then separate as flocculent precipitates in the electrolyte.

AMALGAMS

Attention was directed in the theoretical portion of this work to the fact that, under certain conditions, mixtures of metals—or alloys—could be deposited from electrolytes which contained two or more salts in solution. The electrolytic method of covering metals with brass is an example of the technical application of this method of procedure. It is also employed for analytical purposes ; as when solutions of mercuric chloride are mixed with other metal-salt solutions, in order to obtain the separation of an amalgam. Luckow was certainly the first to carry out experiments in this direction,¹ but it was more especially Vortmann who investigated the electrolytic deposition of amalgams, and who studied the behaviour of many metals towards mercury, when they underwent simultaneous deposition with the latter metal.² The aim of these investigations was to discover whether the amalgam method could not be used to obtain trustworthy results in the case of those metals which in the ordinary way gave unsatisfactory deposits.

Experiments in which the metals are to be separated as amalgams are best carried out—as are depositions of the metal mercury alone—in a platinum basin.

Zinc amalgam.—Luckow recommends a solution of zinc,

¹ *Zeitschr. f. anal. Chem.* 19, 1.

² *Berichte*, 24, 1891, 2752.

made slightly acid with sulphuric acid, to which has been added a solution of an equal weight of mercuric chloride.

If too great an excess of acid be present, the deposition is completely stopped. Vortmann used ammonium oxalate solutions, and also ammoniacal ammonium tartrate solution. When using the former, the zinc and mercury salt solutions were mixed in the proportions of 1 : 2 or 1 : 3 (zinc to mercury); and the electrolysis of this mixture yielded a silvery-white amalgam. In the case of the latter solution the proportion must be at least 1 : 3; otherwise the deposit will be spongy in character. In carrying out such depositions, the weighed amounts of zinc sulphate or chloride and of mercuric chloride are brought into solution, the necessary chemical reagents are added, and the electrolysis is completed as in the case of the single metals. This method of electrolytic determination cannot be recommended for zinc, on account of the injury it causes to the platinum basin. The loss in weight of this can rise to as much as .05 gm. with each single determination.

Cadmium amalgam.—Vortmann has proposed for this the same solutions as those recommended by him for the zinc amalgam. The method with the oxalates can, however, be used only for very small amounts of cadmium, owing to the comparative insolubility of the cadmium ammonium oxalate. When more than .30 gm. of the metal is to be dealt with, the solution containing tartrates is to be preferred. In order to prepare such a solution, cadmium nitrate, or sulphate, and mercuric chloride are dissolved, 3 grms. tartaric acid and excess of ammonium hydrate are added, and after dilution to the usual volume the mixture is electrolysed. If the proportions of cadmium to mercury present in the solution is represented by the ratio 1 : 4 or 1 : 5, the amalgam obtained is hard; if the proportion falls to 1 : 8 the amalgam will be partly fluid.

Lead amalgam.—In order to obtain this amalgam, a solution containing the lead salt and mercuric chloride is mixed with 3 to 5 grms. sodium acetate, potassium nitrite,

and a few cubic centimetres acetic acid. Solutions made slightly acid with nitric acid may also be used ; but the addition of potassium nitrite must still be made, in order to prevent the formation of lead peroxide.

Deposits of amalgams without any formation of peroxide may also be obtained from alkaline solutions containing the two salts, tartaric acid, potassium iodide, and excess of sodium hydrate.

The last method is to some extent an unpleasant one to use, since iodine separates at the anode owing to the decomposition of the potassium iodide ; and this liberated iodine forms gas-holding clots which swim upon the surface of the electrolyte. The lead amalgam when kept dry is stable in the air, but when moist it oxidises very easily. It is therefore necessary to wash the deposit quickly with water and alcohol, to dry it by an air-blast, and to keep the electrode when dry in a desiccator.

The results are satisfactory. Since the method of electrolytic determination by means of peroxide deposition at the anode (see p. 128) is so simple and so entirely satisfactory, the above methods are without practical importance.

Bismuth amalgam.—Bismuth is the metal for the electrolytic determination of which the amalgam method is advantageous ; for if this separation as an amalgam were not feasible in the case of bismuth, only very small amounts of the metal, and even those rarely in the metallic form, could be electrolytically deposited from its solutions.

By use of the amalgam method, amounts up to .60 or .70 grm. bismuth may be separated. The mixed solution of the bismuth and mercury salts may be subjected to electrolysis in various forms.

The ammonium oxalate double salt solution has been found unsuitable for this deposition.

The form of solution in which free nitric acid is present may be used ; the acid must be present in sufficient amount

to keep the basic bismuth salt in solution. Too great an excess of acid, however, causes a deposition of bismuthic acid at the anode. In order to carry out an electrolysis with this solution, .50 grm. bismuth oxide and 2 grms. mercuric oxide are dissolved in the required amount of nitric acid; and the solution of mixed nitrates is electrolysed with currents up to 1 ampère in strength. At the usual temperature this electrolysis requires an E.M.F. of $3\frac{1}{2}$ volts. The relative amounts of the two salts in the electrolyte must be at least 4 of mercury to 1 of bismuth; a silvery-white amalgam will then be obtained. The end of the electrolysis is determined by use of ammonium sulphide. The remaining electrolyte must be displaced by water before the circuit is broken. The washing and drying of the deposit are effected in the usual manner. The bismuth amalgam is not subject to oxidation on exposure to air, and it is little affected by heat. If too little mercury has been used, a black deposit of bismuth will be found covering the amalgam. In order to prevent in all cases the separation of oxygen compounds of bismuth at the anode, a little tartaric acid is added to the electrolyte. These oxides, when they have once separated at the anode, are in most cases not to be brought into solution again.

If a dark band should remain on the platinum electrode after solution of the amalgam, this may be removed by ignition, or by use of the electrode as anode in a dilute nitric acid solution, with a stout copper wire or strip of sheet copper as cathode.

Vortmann has also used solutions containing hydrochloric acid. In order to prepare such a solution, he added potassium iodide and hydrochloric acid to the solution of the bismuth and mercury salts, until a clear liquid was produced. On electrolysis this solution yields a gas-holding scum of iodine upon the surface of the electrolyte. In order to avoid too great an excess of hydrochloric acid when using this method, Vortmann added 50 c.cms. 96 per cent. alcohol

to the solution of the bismuth and mercury chlorides with hydrochloric acid. This addition assists the solution of the chlorides.

The relative proportions of the metals and of the other reagents which should be employed are therefore as follows :— ·20 to ·80 grm. bismuth oxide ; 1 to 2 grms. mercuric chloride ; hydrochloric acid in sufficient amount to dissolve the bismuth oxide ; 50 c.cms. 96 per cent. alcohol. The method yields good results.

In actual work, it is more customary to deposit the bismuth amalgam from the nitric acid solution than from that prepared with hydrochloric acid. The reason for this preference of the nitric acid method—apart altogether from the general objection to the electrolysis of solutions containing chlorides—is to be found in the fact that in the ordinary course of analysis the nitric acid solution is often obtained, or can easily be prepared. It must certainly be held to be a great convenience that in the case of bismuth the amalgam method is sufficiently trustworthy to be used in place of the unsatisfactory methods of obtaining metal separations.

Antimony amalgam.—Formerly the electrolytic determination of antimony was beset with difficulties, and this metal was therefore included in the number of those which it was attempted to separate and to determine as amalgams. The experiments in the case of antimony were made with solutions containing the mixed salts and sodium sulphide. Now that a simple and easy method is known by which it is possible to deposit antimony as metal in sufficiently large amounts and in short periods of time, the amalgam method has become superfluous.

The experiments made upon arsenic salts showed that the deposition of this metal as an amalgam was incomplete.

It is seen from the above that at present the amalgam method of determining the amount of metal in a solution is only of importance in the case of bismuth.

SEPARATION OF THE METALS

In Chapter VII. of Part I. it was shown that when the current is passed through a liquid containing two or more metal salts in solution, the metals are, according to circumstances, deposited either together as alloys or amalgams, or the deposition is only partial, and certain of the metals in the mixture are deposited, while others remain in the solution. The investigation of this phenomenon, in so far as it relates to its application to analytical purposes, is chiefly confined to the discovery of the conditions under which certain metals are deposited separately from mixed solutions. The various separations possible by this mode of procedure may be divided into the four following groups :—

Group I.—Separations of the metals from mixtures containing two or more different metals, by deposition of the one as metal at the kathode, of the other as peroxide at the anode. The separation of copper from lead in a nitric acid solution is an example of an application of the method, which is much used in technical laboratories.

Group II.—Separations of different metals by the maintenance of the electric current used for the electrolysis, at a definite maximum, as regards E.M.F. (ref. p. 35). Since the *decomposition values* of different salts vary, it is possible to effect separations by means of an E.M.F. variable at will, if the two values lie sufficiently far apart.

Kiliani and Freudenberg have shown that if the E.M.F. of the current be kept below that required to effect the electrolysis of the salt with the higher *decomposition value*, the one metal will be deposited, while the other will remain in solution.

Group III.—The separations in this group are effected by artificially increasing the *decomposition value* of the one metal salt. This may be achieved either by raising the salt to a higher level of oxidation, or by converting it into a complex salt through the addition of other salts to the

solution. In either case the metal passes into the anion group on electrolysis ; and its separation from this only occurs in a secondary manner by use of an increased E.M.F., or in some cases does not occur at all.

An example of this class of separation is to be seen in the method adopted to part antimony and arsenic in a sodium sulphide solution. The arsenic is previously raised to the arsenic acid stage of oxidation. As an example of the complex salt method of separation, the parting of iron and cobalt from zinc after addition of potassium hydrate may be cited.

Group IV.—The separation of certain metals from others may be effected by the addition of strong mineral acids to their salt solutions.

In this way the deposition of iron, cobalt, nickel, cadmium, and zinc is prevented. Since those metals are in all cases first separated for which the least E.M.F. is required, it will be the noble metals, gold, silver, copper, and mercury, that are first deposited ; while if a considerable excess of acid be present the remainder of the series of metals given on page 35 will not be deposited, a liberation of the hydrogen of the acid being produced instead.

These methods of separation are not all applicable in the case of every metal ; neither are the four groups given above sharply divided the one from the other in all cases. In many instances a combination of the methods given under two or more of the above groups is used.

For example, one may have a solution containing copper, zinc, lead, and iron for analysis—that is, a solution of a brass containing lead and iron as impurities.

In this case the separation of the copper and lead is effected in a nitric acid solution by the method of Group I. ; but at the same time the copper is being separated from the iron and zinc by the method of Group IV., since these cannot be deposited from a strongly acid solution.

They remain in the electrolyte, and after the copper has been removed they are determined by some special method.

The different separations that are possible will be found described under the headings of the individual metals. The current strengths given in these descriptions of the methods are again based upon a kathode or anode surface area of 100 sq. c.m., even when this is not expressly stated to be the case. In those cases in which no details are given concerning the weights of the salts of the individual metals which are to be used in carrying out these methods, those given in Part III., B, may be taken. Reference to the previous division of the work may also be made in those cases in which nothing is stated concerning the character or the treatment of the metallic deposits.

COPPER

This metal—one of the group known as the noble metals—can very easily be deposited in useful form from solutions containing free mineral acids (ref. p. 93). This characteristic makes the elaboration of a method of separation from the metals zinc, iron, nickel, and cadmium possible, while it also indicates that a separation from those metals which form peroxide deposits at the anode can be carried out.

Copper from Zinc.—The separation of these two metals can be effected in various acid solutions, provided that a sufficient amount of acid be present. The mineral acids are found to yield the best results, and of these, nitric and sulphuric acids are most generally used.

The solution of .50 gm. of each of the salts, zinc sulphate and copper sulphate, is treated with 1 to 2 c.cms. conc. sulphuric acid, diluted to about 150 c.cms. and electrolysed with a current density of between .50 and 1.0 ampère. The E.M.F. required will be from 2.5 to 2.8 volts, and the electrolysis may be carried out either at the normal temperature or at 50° C. The deposition of the copper will be complete in from one and a half to two hours; but the last traces of the copper are difficult to

remove from the solution, and on this account the time required is often greater than that named.

The remarks made on p. 95 concerning the character and the treatment of the deposit apply in this case also.

The remaining acid zinc solution is neutralised after the complete deposition of the copper, and the zinc is deposited by one of the trustworthy methods of electrolytic determination given under "Zinc." If the copper determination has been carried out in the basin electrode, and the liquid displaced before breaking the circuit, it is necessary to evaporate the excess of water, in order that after the addition of the necessary reagents the zinc solution may be electrolysed in the same basin electrode. This is now provided with the required coating of copper, and the weight is already known. If the electrolysis has been conducted in a beaker with the jacket form of electrode, the evaporation of the diluted solution is unnecessary, and the electrolytic deposition of the zinc may be directly proceeded with.¹

Nitric acid may be used in place of sulphuric acid in effecting this separation. In this case the deposition of the copper occurs rather more slowly.

The solution of the two sulphates is treated with about 5 c.cms. conc. nitric acid, diluted to the usual volume, and after heating to about 50° C. it is electrolysed with a current density of from .50 to 1.0 ampère. The E.M.F. required will be between 2.5 and 3.0 volts, and the deposition will demand about three hours.

Since, during the electrolysis of the copper salt, part of the nitric acid is converted into ammonia by the action of the current, a too lengthy duration of the electrolytic separation, or an insufficiency of acid in the solution, may cause the electrolyte to lose its acid reaction through the formation of ammonium nitrate. If this should occur, the zinc may be deposited with the copper.

The liquid containing the zinc salt, after the complete

¹ When a jacket kathode is used, so little wash water is produced that evaporation is unnecessary.

separation of the copper, should not be used directly after neutralisation of any remaining free acid for deposition of the zinc. The presence of nitrates in solution is not favourable to the attainment of good metallic deposits of this metal.

It is most advantageous to evaporate this solution with sulphuric acid, and then to convert the resulting sulphate of zinc into one of the forms given under 'Zinc' as most suitable for the electrolytic deposition of the metal. The further conduct of the electrolytic separation is then exactly as described under 'Zinc.'

Smith has recommended the use of a solution of the sulphate salts of copper and zinc, to which 30 c.cms. of a saturated solution of sodium phosphate, and 3 c.cms. phosphoric acid, have been added.

Very weak currents must be employed with this solution. The copper is deposited first quite free from admixture with zinc. The deposition takes place very slowly, and the method is not so simple as the two methods already described, in which sulphuric or nitric acid solutions are used.

Classen has effected the separation of copper and zinc by means of his oxalate method.¹

The salt solutions of the two metals receive an addition of ammonium oxalate, and are thereby converted into the double oxalate form. The electrolysis is conducted with a neutral or feebly acid solution, and the E.M.F. required is about 2 volts. The method suffers from the disadvantages already discussed under 'Copper' (see p. 100).

The electrolytic method of separation of copper and zinc is made use of in technical laboratories for the analysis of brass. In Part III., D, further reference will be made to this use of the method.

The first-named methods of separation—i.e. those effected in solutions acidified with the mineral acids—are the only two which are of technical importance.

Copper from Iron.—The separation of these two metals

¹ *Berichte*, 17, 2467.

can, in a similar manner to that of the two former ones, be effected in an acid solution, one containing free sulphuric acid having been found to be the most suitable. In order to prepare such a solution of the mixed salts, about 1 grm. each of cupric and ferrous sulphates are dissolved in water, the solution is treated with 3 c.cms. conc. sulphuric acid, and after dilution to 150 c.cms. it is electrolysed at the normal temperature, with a current density of 1 ampère. The E.M.F. required will be from 2.75 to 3.0 volts; the time necessary for the complete deposition of the copper will be from two to two and a half hours. The remaining electrolyte must be washed out of the basin before breaking the circuit; after evaporating to a suitable volume, it is neutralised with ammonium hydrate, and between 4 and 6 grms. ammonium oxalate are added to the solution.

If a jacket electrode is to be used, this evaporation is unnecessary. The electrolysis is carried out at a temperature of 30° to 40° C., with a current density of between 1.0 and 1.5 ampère, and an E.M.F. of from 3.4 to 3.8 volts. The iron will require between three and four hours for complete deposition. The results obtained by this method are good. The ammonium sulphate which results from the neutralisation of the excess acid by ammonium hydrate is without prejudicial influence upon the separation of the iron from the double oxalate salt solution.

If 5 c.cms. conc. nitric acid be added to the solution of the two salts, and, after the usual dilution, the electrolysis be carried out at the normal temperature with a current density of 1 ampère, and an E.M.F. of from 2.9 to 3.3 volts, the complete deposition of the copper will require from four to five hours. The remaining electrolyte must be displaced before the current connections are broken.

If one proceeds, as before, to electrolyse the iron solution after neutralisation of the free acid with ammonium hydrate, and addition of from 4 to 6 grms. ammonium oxalate, a separation of ferric hydrate will occur in the electrolyte during the deposition of the iron. This precipi-

tate of iron can be dissolved by the use of oxalic acid, but such an addition always has a prejudicial influence upon the results, and in very many cases the deposition of the iron is incomplete. It is, on this account, necessary, when a nitric acid solution has been used to effect the separation of the copper, to remove the nitric acid by evaporation with sulphuric acid, before proceeding to this electrolytic separation of the iron.

Classen has used his oxalate method to effect separations of these two metals. The solution containing the two metals as sulphates, together with between 6 and 8 grms. ammonium oxalate in 150 c.cms. water, is treated with oxalic, tartaric, or acetic acid, and small quantities of the acid are added from time to time during the course of the electrolysis in order to maintain the acid reaction of the electrolyte.

The electrolysis is conducted at a temperature of between 50° and 60° C. with a current density of 1 ampère. The E.M.F. required under these conditions will be from 2.9 to 3.4 volts; and the complete deposition of the copper (which separates quite free from iron) will demand about three hours, if 1 gm. copper sulphate has been used.

If sufficient care be not given during the electrolysis to the maintenance of the acidity of the electrolyte, oxalic acid being especially easily decomposed by the current, iron will be deposited with the copper at the kathode. When the deposition of the copper has been completed satisfactorily, the remaining electrolyte may be simply neutralised with ammonium hydrate, and the iron deposited forthwith from this solution at the normal temperature by means of a current of from 1.0 to 1.5 ampère density.

The E.M.F. required will be from 3.0 to 3.3 volts, and the time about three hours. When the iron is to be estimated in this way, only oxalic acid, of those named, may be employed for acidifying the electrolyte during the copper deposition; the electrolysis demands constant supervision, and does not always give satisfactory results.

Vortmann has recommended the use of ammonium sulphate and ammonium hydrate with the sulphate salts of the two metals, when the amount of iron is considerable. A precipitate of flocculent ferrous or ferric hydrate of course occurs in such a solution, but this is said not to be detrimental to the deposit of copper. A current density of between $\cdot 10$ and $\cdot 60$ ampère is employed.

Apart from the objection that exists to the use of solutions containing precipitates in suspension for electrolysis, it is by no means certain that by the use of this method small amounts of iron will not be deposited with the copper.

Smith has also recommended the use of solutions containing sodium phosphate and free phosphoric acid for effecting the electrolytic separation of copper and iron. The remarks made upon this method as applied to the separation of copper and zinc are also applicable in this case.

A consideration of the separate methods described above shows that the method with free sulphuric acid is clearly superior both in simplicity and in reliability to any of the others.

It is necessary to note, in conclusion, that the separation of the two metals copper and iron by the electrolytic method is attended with difficulties when the latter metal is present in considerable amount. This is especially the case when a nitric acid solution is employed. Not only does the already deposited copper partly redissolve, but, according to Schweder, the deposition remains incomplete.¹

Copper from Cobalt or Nickel.—This separation can be effected in a manner precisely similar to that described for the separation of copper from zinc or from iron—namely, by means of solutions of the salts containing an excess of free mineral acids, from which copper alone will be deposited. In this case also sulphuric acid is found to be eminently fitted for use as the acidifying agent. In order to prepare a solution of the mixed salts for electrolysis, 1 grm. each of copper and nickel sulphates (or cobalt sulphate)

¹ *Berg- u. Hüttenzeitg.* 36, 5, 11, 31.

are dissolved in the necessary amount of water, and 3 c.cms. conc. sulphuric acid are added. After dilution to the usual volume the solution is electrolysed with a current density of about 1 ampère at the normal temperature. From two and a half to three hours will be requisite to effect the complete removal of the copper from the electrolyte. The further treatment of the deposit and of the electrolyte is as described under the separations Copper-Zinc and Copper-Iron.

In place of the addition of sulphuric acid, 5 c.cm. of nitric acid may be used, in which case the deposition of the copper occurs under approximately the same conditions as those given above.

In either case the deposit of copper is perfectly free from nickel (or cobalt). Of the two methods, that with sulphuric acid is to be preferred, since, after the electrolyte has been removed from the basin electrode and the washings have been added, it is only necessary to add ammonium hydrate in excess to the solution, now containing only nickel (or cobalt), and to decompose the heated solution by means of a strong current, as described under 'Nickel.'

The nitric acid solution requires a previous evaporation with sulphuric acid in order to convert the nitrate salts into sulphates, if later disturbing influences upon the electrolytic process are to be avoided ; whereas the sulphuric acid solution is, after addition of ammonium hydrate, at once ready for the deposition of the nickel or cobalt.

Classen has recommended the use of the ammonium oxalate double salt, with the addition of oxalic or tartaric acid, for effecting the separation of these metals. A quantitative separation is, however, only possible if the E.M.F. be kept at or below 1.3 volts, since a higher E.M.F. produces an alloy of the two metals at the kathode. This low E.M.F. will only produce a very small current, and consequently the deposition of the copper occupies much time.

Heydenreich has stated that about four hours are requisite to deposit $\cdot 25$ grm. copper.¹

The deposition of copper from a solution of a copper salt to which ammonium oxalate has been added in excess only commences when an E.M.F. of 1.1 volts has been attained, and the margin between this and that named above is extremely small. The conditions are precisely similar in the case of either metal. The oxalate solution when freed from its copper contents may be used directly for the electrolytic separation of the nickel (or cobalt); neutralisation of the free acid by means of ammonium hydrate being alone necessary to prepare it for this further electrolysis. On account of the time required to carry out the deposition of the copper, this method cannot be regarded as a convenient or useful one.

Smith has also recommended the use of his sodium phosphate method for effecting the separation of these metals. The remarks already made concerning this method under Copper-Zinc apply in this case also, and it is unnecessary to repeat them here.

The method of separation of copper from nickel or cobalt by use of a sulphuric acid solution of the metals is the only one of technical importance. It is noteworthy that it was from this solution that Gibbs, in the year 1864, separated the two metals nickel and copper in an examination of 'mint nickel,' and thus gave proof of the applicability of electrolysis to practical analytical purposes.²

Copper from Cadmium.—One would suppose that cadmium, which as regards both its chemical and its electrolytic characteristics and properties stands closely allied to zinc, would show a similar relationship to zinc in the manner of its separation from copper, and that the addition of the required amount of free mineral acid to the solution of the two salts would suffice to effect an easy separation of copper from cadmium. This supposition is, however, correct only

¹ *Zeitschr. f. Elektrochem.* 1894, 1, 290.

² *Zeitschr. f. anal. Chem.* 3, 334.

to a very limited degree. The deposition of the copper occurs satisfactorily when nitric acid solutions are made use of. In order to carry out such a separation .30 to .50 gm. cadmium sulphate is dissolved with 1 gm. copper sulphate in water; the mixed solution receives an addition of 5 c.cms. nitric acid, and after dilution to 150 c.cms. it is electrolysed at the normal temperature with a current density of from .80 to 1.0 ampère. The E.M.F. required will be from 2.8 to 2.9 volts; the deposition of the copper will demand about four and a half hours. Equally good results can be obtained if 10 c.cms. nitric acid be used, and if the electrolysis be carried out during the night with a small current density of from .20 to .30 ampère, by means of an E.M.F. of from 1.9 to 2.2 volts. When this method of procedure is adopted, it is necessary to increase the current to a density of at least 1 ampère the next morning, in order to effect the separation of the last traces of copper from the solution. The displacement of the remaining electrolyte must occur before the current connections are broken.

If it be desired to effect the determination of the cadmium in this solution, it is made alkaline with sodium hydrate, and is then treated with a freshly prepared solution of pure potassium cyanide until the first-formed precipitate is redissolved.

The electrolytic deposition of the cadmium is then carried out as described under 'Cadmium.'

If the ammonium oxalate double salt solution be preferred for use in obtaining the cadmium deposit, it is necessary to evaporate the solution from the first part of the analysis with sulphuric acid, in order to convert the nitrates into sulphates, since the presence of the former leads to incomplete and unsatisfactory deposit when the double oxalate method is employed. The solution of sulphates obtained in this way is neutralised with ammonium hydrate, 8.0 grms. ammonium oxalate are added, and the solution made up to the proper volume is then electrolysed with a

current of from .50 to .80 ampère density at a temperature of 60° C., with the precautions relative to the presence of oxalic acid described at length under 'Cadmium.'

The two metals may also be separated in a solution containing sulphuric acid in place of nitric acid, but this separation is not possible in such solutions under all circumstances.

If, for example, a solution be prepared containing .30 grm. cadmium sulphate, 1.0 grm. copper sulphate, and 3 c.cms. conc. sulphuric acid in 150 c.cms. water, and this be electrolysed, as in the case of the nitric acid solution, at the normal temperature with a current of 1.0 ampère density, an alloy of the two metals, copper and cadmium, will be obtained at the kathode.

Under the above circumstances the E.M.F. will be about 2.8 volts. If, however, the E.M.F. be not allowed to exceed 2 volts, and if the electrolysis be accordingly undertaken with a weaker current, it is quite possible to obtain a deposition of copper quite free from cadmium. In this case the electrolysis should be carried out at a temperature of 60° C. ; the separation under these conditions lasts about eight hours.

The solution containing sulphuric acid that remains when the deposition of the copper is completed, after neutralisation, may be *directly* used for the deposition of the cadmium, either by the potassium cyanide or the ammonium oxalate method. One may, however, in this case make use of a third method, and electrolyse the cadmium sulphate solution, after neutralisation with ammonium hydrate, and without the addition of any other reagents, with a current of 1 ampère density at a temperature of between 50° and 60° C. The E.M.F. required will be from 3.0 to 3.5 volts, and the deposition will demand between three and a half and four hours. The deposit of cadmium obtained will be bright and metallic.

If between 5 and 6 grms. pure potassium cyanide be added to a solution of the sulphates of copper and cadmium, of which each is present in an amount equivalent to

·50 gramm. of the metal, and if this solution after dilution to between 130 and 150 c.cms. be electrolysed with a current produced by an E.M.F. not exceeding 2·6 volts, Smith and Freudenberg state that cadmium alone will be deposited, while copper will remain in solution.¹ It is therefore possible to effect a separation in this manner.

It is remarkable that in this case the 'decomposing values' of the complex cyanides of copper and cadmium do not follow the order of those of the neutral and acid salts (see p. 46).

From solutions which contain a mixture of the double oxalates of these two metals, a separation cannot be effected by the use of moderately strong currents. It is, however, not impossible that by the use of an E.M.F. not exceeding 2 volts a separation might be obtained in such solution. The separation of copper from cadmium in solutions containing sodium phosphate and free phosphoric acid is possible when extremely weak currents are employed. The deposition of the copper demands about twelve hours, and this fact alone places this method far behind the others as regards convenience or usefulness.

The most simple and convenient method to use for effecting separation of copper and cadmium is that depending upon the use of a nitric acid solution of the mixed salts.

Copper from Aluminium, Magnesium, Chromium, Calcium, Barium, Strontium, Potassium, and Sodium.—The separation of copper from these metals is effected without difficulty, if the electrolysis be carried out with solutions containing a sufficiency of sulphuric or nitric acid, and under the current conditions mentioned by Copper-Zinc and Copper-Iron.

Copper from Lead.—The separation of copper from lead is easily effected in a nitric acid solution, for out of such solutions copper is deposited in bright metallic form at the kathode, whereas lead is separated as peroxide at the anode.

If a solution containing these two metals has received

¹ *Jour. anal. u. appl. Chem.* 3, 385.

an addition of the requisite amount of nitric acid, the electrolysis will result in the deposition of each metal at the opposite electrode, and numerous experiments have proved that the separation is absolutely complete. In order to carry out such an electrolysis, 1 grm. each of copper and lead nitrate is dissolved in water, 15 c.cms. of conc. nitric acid are added to the solution, and the clear mixture is then diluted to 150 c.cms. If copper sulphate should be used in place of the nitrate, a white precipitate of lead sulphate will be formed on adding the lead nitrate, and this compound can only be brought into solution by gentle heating with an excess of ammonium hydrate.

If this method has been used it will be necessary to neutralise with nitric acid, before adding the measured quantity of acid named above. The solution, which must be perfectly clear, is heated to 60° F., and the current connections are then made in such a manner that the larger electrode surface, i.e. the platinum basin or cone, functions as anode for the reception of the deposit of lead peroxide. The remarks made under 'Lead' relative to the advantage of using a well-worn electrode apply of course with equal force in this separation. The current density required will be from 1.0 to 1.5 ampères; the E.M.F. will be only 1.4 volts.

One hour will suffice to complete the separation of all the lead as peroxide at the anode, but a longer period will be requisite to complete the deposition of the copper, since it has always been observed that when the electrolysis is first commenced only the peroxide is separated, and that the deposition of the copper commences later and takes place more slowly. After the whole of the lead is deposited the current connection is broken, there being no necessity at this point to pay any attention to the fact that the greater portion of the copper is still in solution. If the jacket electrode has been used, it is simply necessary to lift this with its coating of peroxide out of the solution, and to wash and dry it as described fully under 'Lead.' A new jacket electrode is then fixed in position in the solution,

which is now free from lead, but the current connections are reversed, and the cone now functions in the usual manner as kathode.

The copper which in the previous electrolysis had separated upon the electrode that is now acting as anode is redissolved in the electrolyte, and is separated with that which originally remained in solution upon the new kathode.

If a basin electrode has been used, the electrolyte must be displaced before the current connections are broken when the whole of the lead has been separated as peroxide ; and the deposit of the latter must be treated as already described. The displaced liquid together with the wash water is evaporated down to a volume of about 130 c.cms., and after neutralisation with ammonium hydrate 10 c.cms. nitric acid are again added in order to raise the electrolyte to the degree of acidity required.

The electrolysis of the copper salt is then carried out at the normal temperature with a current density of 1.0 ampère, and an E.M.F. of from 2.2 to 2.5 volts. In this case a fresh platinum basin is used as kathode ; while the disc electrode with its deposit of copper obtained during the deposition of the lead peroxide is now used as anode, and speedily loses its coating of copper. The time required to effect the deposition of the whole of the copper will be from four to five hours. The simplest test to apply in order to ascertain whether all the lead has been deposited as peroxide in the first portion of this electrolysis, is to add a little to the volume of the electrolyte, and to watch the freshly covered anode surface for traces of a deposit of the dark-coloured lead peroxide. The deposit of copper obtained in the second part of the separation is washed and dried in the usual manner.

This method for effecting the separation of copper and lead is one which has attained a very wide field of usefulness in technical laboratories.

Copper from Manganese.—The latter metal is deposited, as already noticed, from nearly all its solutions in the form

of peroxide, but this deposition occurs with especial ease and certainty in the case of solutions containing a little free sulphuric acid. If copper be present in such a solution, it would reasonably be assumed that on electrolysis this metal would be deposited at the kathode, while the manganese would be found at the anode, i.e. a separation might be expected to occur. This supposition is found to be correct, for such a separation does occur, and is complete. In order to carry out this electrolysis, .50 grm. each of copper and manganese sulphates (or nitrates) are dissolved in water, and after dilution of the solution to between 130 and 150 c.cms. ten drops of conc. sulphuric acid are added. The mixture is then heated to 50° to 60° C., and is electrolysed with a current varying between .50 and 1.0 ampère in density. The electrolysis will require between two and three hours. The remarks made concerning the use of the larger electrode for the reception of the lead peroxide deposit under 'Copper-Lead' apply here, as do those also made under 'Lead,' concerning the use of a well-worn electrode surface. It is not advisable to use a larger amount of the manganese salt than that named above, since there is some danger of the manganese deposit scaling.

The deposit of manganese peroxide after washing and drying is ignited and weighed, the results being calculated upon the formula Mn_3O_4 . Equally reliable results may be obtained by drying the manganese peroxide deposit at 60° C., and by using the formula $MnO_2 + H_2O$ in the after calculation. In this case the factor .523 is used to convert the weight of the deposit into its equivalent of Mn. The deposit of copper obtained simultaneously at the kathode is treated in the usual manner.

Since manganese may be deposited as peroxide from a solution containing free nitric acid, a form of solution from which copper also may be obtained in very satisfactory deposits, it is possible to separate these two metals in solutions containing a small amount of free nitric acid. A few c.cms. nitric acid are added to the diluted solution of the

two salts, and the mixture after heating to 50° C. is electrolysed with a current density of about .50 ampère.

The deposition will be complete in three hours. The use of high-current densities is not recommended, on account of the detrimental effect of these upon the coherence of the deposit of manganese peroxide. The other conditions of the separation by this method are similar to those described above.

If the amount of free nitric acid present be allowed to exceed 3 to 4 per cent., no deposition of manganese peroxide will take place at the anode, a formation of red permanganic acid will occur in its stead.

Smith has used solutions containing 30 c.cms. saturated sodium phosphate solution, and 10 c.cms. phosphoric acid, in order to effect separations of copper and manganese. If very feeble currents be employed with such solutions, the copper alone is deposited, while the manganese remains completely in solution. The two methods first named, however, excel Smith's method not only in simplicity but also in speed.

Classen has proposed his double oxalate method for separating copper and manganese.

The extremely slight adherent properties shown by the manganese deposit obtained from these solutions, together with the unsatisfactory character of the copper deposit, place this method also, in respect to simplicity and reliability, far behind the two methods first described.

Copper from Silver.—The principal factors in the development of the fairly simple methods for the separation of copper from the other metals that have hitherto been described have been the properties displayed by certain metals which, on electrolysis of their salt solutions, yield peroxides at the anodes, and of others which yield no deposit at all when the electrolysis is carried out in acid solutions. In effecting the separation of copper from the metals silver, mercury, bismuth, &c., the 'decomposition values' of whose salts lie very close to those of the

salts of copper, it is necessary to attempt to bring about a separation by the employment of an E.M.F. lying midway between those represented by the 'decomposition values' of the two salts concerned ; or, if this be impossible, an attempt must be made to bring about a greater divergence in these values by use of other forms of solution.

The separation of copper and silver can be undertaken in different solutions. Freudenberg¹ and Kiliani² have shown that these metals may be separated in nitric solutions when the E.M.F. is not allowed to exceed 1.3 or 1.4 volts.

In order to effect such an electrolysis, the metals may be dissolved in nitric acid, or .5 gm. of each of the neutral nitrate salts is dissolved in water, and after addition of 2 to 3 c.cms. nitric acid, and dilution to the usual volume, the electrolysis is carried out by means of the E.M.F. named above. The current-density obtained with this E.M.F. will only be .10 ampère ; and the deposition of silver will require six to seven hours at the normal temperature, or three to four hours if the electrolyte be heated. The remaining electrolyte is removed from the basin electrode by a syphon, and after addition of the washings the volume is reduced within the required limits by evaporation. The copper deposition is then effected in this solution after the addition of a few cubic centimetres of nitric acid, with a current density of from .50 to 1.0 ampère. The time required will be between one and two hours.

If a cone electrode be used, the evaporation of the solution may be avoided, and in this case one merely fixes a fresh electrode in the beaker containing the electrolyte and the washings, after addition of the necessary amount of nitric acid, and proceeds with the electrolysis with a stronger current. If the E.M.F. be allowed to exceed that mentioned above, an alloy of the two metals will be

¹ *Zeitschr. f. phys. Chem.* 1893, 12, 197.

² *Berg- u. Hüttenzeitg.* 1883, 375.

obtained at the kathode. This method of separation is simple, and yields very satisfactory results.

Smith and Frankel¹ and Smith and Spencer² have used solutions of the double cyanides for this purpose. In order to prepare such a solution, between 1 and 2 grms. of pure potassium cyanide is added to the neutral solution of the two salts, which must be present in amount equal to .40 to .50 grm. metal, and after dilution to the usual volume (150 c.cms.) the electrolysis is carried out with currents up to .10 ampère in density.

If the deposition be carried out at the normal temperature from eight to twelve hours will be requisite to effect the complete separation of the silver; if the solution be heated to 60° C., the whole of the silver can be deposited in four hours. Freudenberg has found that the E.M.F. must not be permitted to exceed 2.3 to 2.4 volts, otherwise the copper will be deposited with the silver; a fact also discovered by Smith and Frankel in experiments carried on with very small current strengths. The addition of potassium cyanide may certainly be increased in amount. Under the conditions given, the deposit of silver is obtained perfectly free from copper. The latter metal is deposited from the remaining electrolyte simply by increasing the current density. The details of the procedure will be found under 'Copper.'

Classen has recommended his oxalate method for effecting the separation of copper and silver. The addition of ammonium oxalate solution to a solution of the salts of these two metals produces precipitates of their oxalates, one only of which—copper oxalate—is soluble in excess of the reagent. The separation is therefore not an electrolytic but a chemical one, and there is the disadvantage that the deposition of copper from its double oxalate solution is never satisfactory. In order to effect the electrolytic depo-

¹ *Amer. Chem. Jour.* 12, 104.

² *Zeitschr. f. Elektrochem.* 1894, 542; *Elektrochem. Zeitschr.* 1894, 186.

sition of the silver, the silver oxalate precipitate must be dissolved in potassium cyanide, and the solution thus obtained then electrolysed in the usual manner.

A further disadvantage of this method is that the precipitate of silver oxalate carries with it some copper, which cannot be redissolved by the ammonium oxalate. It follows therefore that this method stands far behind the two methods first described as regards simplicity and accuracy.

The electrolytic method of separating copper and silver could receive a practical application in the analysis of silver coinage-metal, and this use of it will receive further notice in Part III., D.

Copper from Quicksilver.—According to Smith, the separation of these two metals can be effected in solutions of the double salts with potassium cyanide.¹ In order to carry out such an electrolysis from .50 to 1.0 gram. copper sulphate, and at the most .50 gram. mercuric chloride, are dissolved in water, and to this solution from 2.0 to 4.0 grms. pure potassium cyanide are added. The clear solution after dilution to the usual volume is electrolysed with a current density of from .06 to .08 ampère.

At the normal temperature about sixteen hours will be found necessary to effect the separation of the mercury; if the electrolyte be heated to 60° C., the deposition of this metal can be effected in from three to four hours. The mercury separates as a dead silver-white deposit, and is perfectly free from copper if, as Freudenberg has pointed out, the E.M.F. be kept below 2.5 volts. If the E.M.F. should exceed this limit, copper will separate with the mercury at the kathode.

The copper may be directly deposited from the cyanide solution by use of a stronger current, or the cyanides may be destroyed by heating with sulphuric acid (under a draught-hood), and the copper then separated electrolytically from the resulting sulphuric acid solution.

¹ Electrolyse.

Copper from Bismuth.—The separation of these two metals in a solution containing nitric acid is not possible, since the 'decomposing values' of their salts lie too closely the one to the other. Smith effects their separation by using a solution of the bismuth salt to which 3 or 4 grms. citric acid have been added, followed by an excess of sodium hydrate solution.

The separately prepared solution of the double cyanide of copper and potassium is then added to this mixture. Bismuth does not form a double cyanide. During the electrolysis of this solution of the mixed salts, the E.M.F. must not be allowed to exceed 2·7 volts, otherwise the bismuth deposit will contain copper.

On account of the very small current density—about ·05 ampère—which it is possible to employ, not more than ·20 gm. bismuth can be deposited in twenty-four hours.

Copper from Arsenic.—The earlier experimenters who attempted to separate these two metals in acid solutions always obtained deposits of copper contaminated with arsenic. Freudenberg was the first to show that a copper deposit perfectly free from arsenic could be obtained from a solution containing between 10 and 20 c.cms. dilute sulphuric acid, if an E.M.F. of 1·9 volts be not exceeded for production of the current passed through the electrolyte. Though similar results could be obtained with nitric acid solution, those containing sulphuric acid are to be given the preference. According to Drossbach,¹ McKay,² and Oettel,³ copper can also be obtained as a bright metallic deposit, completely free from arsenic, by use of very feeble currents, and ammoniacal solutions of copper (see under

Copper,' p. 98) in which the arsenic may be present either in the arsenious or arsenic form of combination. The explanation of this lies in the fact that arsenic is an element which possesses both basic and acid properties in its combinations, and that in alkaline solutions the arsenic

¹ *Chem. Zeitg.* 1892, 819.

² *Ibid.* 1890, 509.

³ *Ibid.* 1894, 879.

forms part of the complex anion, and does not exist separately as an ion.

Arsenic acid and the arsenates especially are only reduced with difficulty, and on this account it is advisable to convert any arsenic that may be present into this form of combination by means of nitric acid, and afterwards to make the solution alkaline. The oxidised solution of the two metals is treated with 30 c.cms. ammonium hydrate, and this alkaline solution is then decomposed by a current, the E.M.F. of which should not exceed 1.9 volts. The deposition of the copper will require from six to eight hours.

The deposit obtained in this way will be perfectly bright, whereas a deposit of copper containing arsenic has always a more or less dirty or black appearance. The arsenic that remains in the electrolyte after complete separation of the copper must be determined by gravimetric methods of analysis, since no electrolytic method is applicable for this metal.

Smith has stated that a precisely similar method of separation to that just described for ammoniacal solutions is applicable to potassium cyanide solutions. The mixed solution of the copper salt and the alkali metal arsenate is treated with an excess of potassium cyanide, and after dilution is electrolysed with a very feeble current.

A deposit of copper quite free from arsenic is also obtained in this case.

Copper from Antimony and Tin.—If one attempts to separate these metals by means of a current of moderate density in an acid solution, it will be found that both metals are deposited simultaneously at the kathode. Copper is, however, deposited alone when the E.M.F. does not exceed 1.8 volts ; and it is therefore possible to obtain a deposit of copper free from antimony, especially when the amount of the latter metal present is small, if the electrolysis be not allowed to continue for too long a period—that is, if it be stopped as soon as the whole of the copper is removed from the solution. Such a method of separation cannot, however,

be recommended. Antimony is a metal that resembles arsenic in its behaviour in alkaline solutions. One can therefore separate copper and antimony in an ammoniacal solution, especially if the precaution be taken to raise the antimony salts present to the higher stage of oxidation by means of nitric acid. If this precaution be omitted, antimony may be deposited at the kathode with the copper, as in the case of an antimony trichloride solution, which has simply been treated with excess of ammonium hydrate. Schmucker has effected the separation by this method, by using an oxidised solution of the two metals to which 8 grms. tartaric acid and 30 c.cms. ammonium hydrate have been added.¹ The electrolysis is carried out with a current of .10 ampère density, and five hours is requisite to deposit .10 grm. copper. The latter metal will be obtained quite free from antimony.

This method may also be used to effect the separation of copper and tin. The separation of copper from antimony and tin by electrolytic methods is not, however, of any technical importance, since this separation is so easily effected by the chemical method with nitric acid.

LEAD

Lead from Copper.—(See p. 177.)

Lead from Silver.—Lead is deposited as peroxide at the anode from solutions containing free nitric acid ; and it is therefore possible to effect separation of lead from those metals which are deposited at the kathode from such solutions. The method of separation of copper from lead is based upon this principle, but when one employs a similar method to effect the separation of silver and lead the silver exhibits a disturbing characteristic, in that under certain conditions it separates partly at the anode as peroxide. This, of course, prevents any quantitative separation of the two metals, for the lead peroxide deposit is contaminated with silver.

¹ *Jour. Amer. Chem.* 15, 195.

Since it is possible, however, under certain conditions (see 'Silver') to obtain deposits of this metal by use of nitric acid solutions without any separation of silver peroxide, investigations have been made to discover the conditions which regulate the deposition of the silver in presence of lead. Luckow has stated that these are the presence of at least 18 per cent. free nitric acid, and the addition of a small amount of oxalic acid.¹ With such an electrolyte the lead peroxide obtained at the anode is free from silver. Smith and Moyer state that if 15 c.cms. nitric acid be present to each 180 c.cms. of the solution, and if a feeble current be used, equally good results may be obtained. In spite of these results this method of separation for silver and lead cannot be regarded as absolutely trustworthy.

Lead from Bismuth.—In the attempts that have been made to effect the electrolytic separation of these two metals, the same phenomena are found to occur as in the case of silver and lead. The bismuth is deposited always, partly as metal at the kathode, and partly as peroxide at the anode. No separation is therefore possible in a nitric acid solution; the lead peroxide deposit, according to Classen and Ludwig,² and Smith and Moyer,³ always contains bismuth.

Lead from Mercury.—Although in nitric acid solutions lead is always deposited as peroxide, while mercury is always obtained as metal, it is not always possible to effect a separation of these two metals in such a solution. If less than a 15 per cent. excess of free nitric acid be present, and if moderately strong currents be used, Smith and Moyer state that part of the lead will be deposited as an amalgam at the kathode.⁴ According to Heydenreich, the conditions necessary in order to obtain a complete separation of lead and mercury are—the presence of between 20 and 30 c.cms. free nitric acid in the 150 c.cms.

¹ *Zeitschr. f. angew. Chemie*, 1890, 345.

² *Berichte*, 19, 326.

³ *Jour. f. anal. u. appl. Chem.* 1893, 7, 252.

⁴ *Ibid.* 1893, 7, 252; *Zeitschr. f. anorg. Chem.* 4, 267.

volume of the electrolyte, and the use of a current of about 20 ampère in density.¹

Lead from Arsenic.—If a solution containing lead nitrate, a soluble salt of arsenic acid, and free nitric acid be electrolysed, the separation of the lead as peroxide at the anode will be found to be nearly always incomplete.

The deposit obtained during the same time at the kathode will be a mixture of arsenic and lead, while another portion of the arsenic will be evolved at the kathode surface as arseniuretted hydrogen.

The greater the amount of arsenic in the solution, the less will be the amount of lead separable at the anode as peroxide; the excess of nitric acid present also affects this result. If the electrolysis be continued, after all the lead has been separated from the solution either as metal at the kathode or as peroxide at the anode, part of the former redissolves and migrates to the anode, where it is deposited as peroxide; but the author has made experiments which prove that the separation of the lead at the anode is never complete.²

Lead from Manganese.—From acid solutions manganese separates as peroxide at the anode, and, since lead yields a similar deposit in nitric acid solutions, one would surmise that the electrolysis of a solution of the mixed salts of these metals containing free nitric acid would yield a mixed deposit of peroxides at the anode. This is found by experiment to be the case. If the excess of nitric acid added to the electrolyte be, however, over 4 per cent., no deposition of manganese peroxide occurs at the anode; in place of this there is a formation of permanganic acid, recognisable by the pink coloration which it produces round the anode. If a solution of the two salts containing about 20 per cent. nitric acid be electrolysed at the normal temperature by means of a weak current, the deposition of lead peroxide will take place slowly, and the solution will

¹ *Zeitschr. f. Elektrochem.* 1896, **3**, 151.

² *Chem. Zeitg.* 1896, **20**, No. 39.

remain colourless. If, however, the electrolyte be heated to 60° or 70° C., and the electrolysis be carried out with a current of from 1·5 to 2·0 ampères in density (E.M.F. 2·5 to 2·7 volts), the whole of the lead will be deposited as peroxide in a short time, and the liquid will assume a rose colour owing to the formation of permanganic acid and its salts. The method yields approximately accurate results when carried out as described above, and when the amount of manganese present does not exceed ·03 grm. for 150 c.cms. of the electrolyte. If the manganese present exceeds this amount, or if the electrolysis be permitted to continue for too long a time, the author has found that a flocculent precipitate of a hydrated manganese peroxide is formed, and that the lead peroxide deposit is no longer free from the other metal.¹

Lead from Zinc, Iron, Nickel, Cobalt, and Cadmium.—Lead can be separated in a very simple manner from all those metals—placed above hydrogen in the list given on p. 35—which cannot be deposited in acid solutions. The solution of the mixed salts simply requires to be acidified with 15 to 20 per cent. conc. nitric acid, and to be electrolysed with the current conditions given under ‘Lead’ (see p. 128).

Lead peroxide will be deposited at the anode, while the other metal remains in solution. The separation is complete. After deposition of the whole of the lead, the remaining liquid, which will still contain much free nitric acid, is treated with the chemical reagents necessary to produce the salt of the metal present, that is recommended for use under the single metal separations. In few cases only is neutralisation sufficient; and a conversion of the nitrates into sulphates will be found to be necessary in the greater number of instances.

¹ *Chem. Zeitg.* 1896, 20, No. 39.

SILVER

Silver from Copper.—(See p. 181.)

Silver from Lead.—(See p. 187.)

Silver from Bismuth.—Freudenberg has stated that if a solution of the nitrates of silver and bismuth (about .30 gm. each metal) be treated with 2 to 3 c.cms. nitric acid, and, after addition of 2 to 4 grms. ammonium nitrate and dilution to 150 c.cms., the mixture be electrolysed with a current the E.M.F. of which does not exceed 1.3 volts, an electrolytic separation of these two metals will be obtained. If the electrolysis be permitted to continue through the night, .30 to .40 gm. silver may be easily deposited. The remaining electrolyte which contains the bismuth is used for the deposition of the latter by the amalgam method.

Silver from Mercury and Gold.—This separation cannot be effected either by the use of nitric acid solutions or by the use of cyanide solutions, since the 'decomposition values' of these salts of the concerned metals lie too close one to the other.

The electrolytic determination of silver and mercury may, however, be carried out as follows. The two metals are deposited together from a solution at the normal temperature by means of a current of .50 ampère density. The E.M.F. required will lie between 1.7 and 2.2 volts; and for .30 gm. silver about four and a half hours will be necessary to effect complete deposition. After drying, the weight of the combined metals on the electrode is determined; the mercury is then driven off by ignition, and the weight of the remaining silver obtained. The deposit of the two metals is grey in colour and spongy in character; but in spite of this the method yields correct results.

Silver from Antimony and Arsenic.—The separation of silver from these metals is possible by electrolytic methods if solutions containing free nitric and tartaric acids be used, and if the antimony and arsenic present be previously raised by chemical methods to the higher stage of oxidation.

Under these conditions it is not safe, however, to exceed an E.M.F. of 1.5 volts.

The deposit of silver obtained is not very well suited for correct weighing. In the case of arsenic the E.M.F. used may be slightly greater than in the case of antimony ; but 1.7 volts must not be exceeded even in this case.

Silver may also be separated from arsenic and antimony in a solution which contains free ammonium hydrate and ammonium sulphate, since from such a solution silver can be deposited by means of an E.M.F. of 1.20 or 1.30 volts. This low E.M.F. causes, however, the deposit of silver to be but loosely adherent to the platinum basin.

The separation of these metals may also be carried out with solutions containing 1.0 gm. pure potassium cyanide for each .10 gm. metal present. Freudenburg has stated that from such a solution the silver can be obtained as a firmly adherent deposit. The E.M.F. used may be somewhat higher than in the case of the nitric acid solution, but it must not exceed 2.4 volts. As before, it is best to raise the arsenic and antimony to the higher stage of oxidation before commencing the electrolysis. Smith states that the separation of silver from these metals by this method succeeds perfectly when tartaric acid is used in excess in the solution.¹

Silver from Platinum and Palladium.—In order to effect the separation of silver from the first of these metals, the solutions of their mixed salts is neutralised, and after the addition of 2 or 3 grms. potassium cyanide it is electrolysed with a current, the E.M.F. of which does not exceed 2.50 volts.

The separation of silver from palladium is not possible in this way.

Silver from Cadmium, Zinc, Cobalt, Nickel, and Iron.—The separation of silver from the metals which cannot be deposited in an acid solution, of which those named above are examples, is conveniently carried out by

¹ *Amer. Chem. Jour.* 12, 428.

electrolysis of the solution of the mixed salts, after acidifying with nitric acid.

The E.M.F. used should lie between 2·0 and 2·2 volts.

Solutions of the double cyanide salts containing an excess of potassium cyanide (2 to 3 grms. pure KCN) may also be used to effect the separation of silver from the metals named above.

This method is to be preferred to that first described since the deposit of silver obtained by it is more satisfactory. The separation of silver from zinc can be effected in such a solution if the E.M.F. used does not exceed 2·5 volts. The current density possible with this E.M.F. is between ·05 and ·08 ampère ; the temperature should be 60° C. The same conditions apply in the separation of silver from nickel, but in this case if the electrolysis be allowed to continue for too long a period nickel may be deposited with the silver. The presence of a cobalt salt in the electrolyte renders it more difficult to effect the separation of the silver ; and in this case the E.M.F. used may rise to a maximum of 2·7 volts. In the case of cadmium the 'decomposition values' of the two double cyanide salts lie very near together, and in order to obtain the silver free from cadmium it is necessary to use an E.M.F. of only 1·9 volt. The current obtained by use of this E.M.F. will be only ·04 ampère in density.

In all these cases it is best to use the solutions at a temperature of between 50° and 60° C. In order to determine by electrolytic methods the amount of the second metal in the solution, it is necessary after complete deposition of the silver to treat the remaining electrolyte with sulphuric acid under the draught-hood, and then to apply the method which is most strongly recommended for the concerned metal in Part III., B.

MERCURY

This metal is closely related to silver in its electrolytic characteristics ; and its separation from the other metals

is effected by methods very similar to those used for silver. In nitric acid solutions an E.M.F. of only 1.3 volts suffices to produce a deposit of mercury.

Mercury from Copper.—See p. 184.

Mercury from Lead.—See p. 188.

Mercury from Silver.—See p. 191.

Mercury from Bismuth.—In spite of all assertions to the contrary, the separation of these two metals can be effected in solutions of their nitrates containing an excess of nitric acid, if, as Freudenberg has pointed out, the E.M.F. of the current used does not exceed 1.30 volt.

Although the current density obtained with this E.M.F. is extremely small, and as a consequence the time demanded for the electrolysis is rather long, the method is a practicable one. The deposit of mercury obtained is not composed of minute globules, but is a smooth metallic coating.

If stronger currents be used the two metals will be simultaneously deposited as an amalgam, a fact which is made use of in the electrolytic method for determining bismuth.

Mercury from Arsenic and Antimony.—The separation of mercury from these two metals can be effected, if the electrolysis be carried out with solutions containing free nitric acid by means of currents, the E.M.F. of which does not exceed 1.8 volts. A solution of the mixed salts containing tartaric acid and an excess of ammonium hydrate may also be used, if the arsenic and antimony are present in the form of their higher oxides.

The current conditions in this case are as above. In order to carry out such a separation, the chlorides are dissolved with the addition of 1 gram. tartaric acid, the solution is diluted, and after neutralisation with ammonium hydrate a further 20 c.cms. of this reagent is added. The mixture is then electrolysed by a current the E.M.F. of which is kept between 1.60 and 1.70 volts.

In order to determine the antimony in the electrolyte remaining when the first method is used, the excess of

nitric acid must be carefully evaporated, and sulphuretted hydrogen then passed through the diluted solution. The precipitate of antimony pentasulphide is then dissolved in sodium sulphide, and the electrolysis of the resulting solution is conducted as described under 'Antimony.'

Mercury from Tin.—It was stated under 'Mercury' that it was possible to completely deposit that metal from the alkaline solutions of its sulphide in sodium sulphide, while under 'Tin' it was noted that the latter metal could not be deposited from such solutions. A method of separation may therefore be based upon this difference.

If both metals be present in solution in presence of free alkali and excess of sodium sulphide, it is merely necessary to employ the current conditions given under 'Mercury' (see p. 142) in order to obtain a complete separation. The remaining electrolyte containing the tin must be boiled with 30 grms. ammonium sulphate, in order to convert the sodium sulphide into ammonium sulphide before the deposition of the tin can be proceeded with. This method of depositing tin will be found more fully described under 'Antimony and Tin' (see p. 201).

A separation of mercury from tin can also be effected by the method with tartaric acid and ammonium hydrate described under 'Mercury and Antimony.' In this case, a few grams tartaric acid and 30 c.cms. ammonium hydrate are added to the mixed salts solution, and the electrolysis is carried out with a feeble current and an E.M.F. not exceeding 1.70 volts.

Mercury from Gold.—This separation can only be effected in solutions containing an excess of potassium cyanide by means of currents the E.M.F. of which does not exceed 1.90 volts. It is also necessary that the electrolysis should be stopped when all the mercury is deposited, otherwise the mercury deposit will be found to contain some gold. Smith states that the deposition of the mercury under these conditions is extremely slow.¹

¹ *Amer. Chem. Jour.* 11, 264, 352; 12, 428; 13, 417.

Mercury from Palladium, Platinum, and Osmium.—If the solution of the salts of any one of these metals and mercury (·20 grm. of each metal) be treated with an excess of potassium cyanide, and then be electrolysed with a current of ·20 ampère in density, a separation of the metals will be found to occur.

The mercury will be obtained as a deposit at the kathode, whereas the other metal will remain in solution. According to Smith,¹ and to Smith and Frankel,² the separation requires from fourteen to sixteen hours.

Mercury from Manganese.—From a solution containing free sulphuric acid, mercury can be separated as a metal and manganese as peroxide. This form of solution can therefore be used to effect the separation of these two metals. The electrolysis is carried out under the conditions described under 'Manganese.' It is, however, necessary to note here that only very small amounts of either metal must be present in the solution, on account of the tendency of large amounts of manganese to separate from such solutions in a non-adherent form at the anode. The use of the larger electrode surface as anode does not remove this difficulty. With regard to mercury, the deposition of larger amounts is attended by a running together of the minute globules and formation of small balls, which are easily detached from the kathode surface.

Mercury from Iron, Cadmium, Nickel, Cobalt, and Zinc.—The separation of mercury from these metals can be effected by the method used to separate copper and silver from the same group of metals—namely, by the electrolysis of a nitric acid solution. The E.M.F. used to effect the deposition of the mercury in such a solution may rise to a maximum of 2·4 volts. The deposition occurs easily, and the separation is complete.

The remaining solution after deposition of the whole of the mercury should be treated with sulphuric acid in order to convert the nitrates into sulphates, since only in few cases can a nitrate solution be used without harmful results

¹ *Amer. Chem. Jour.* 11, 264, 352; 12, 428; 13, 417. ² *Ibid.* 12, 428.

for the electrolytic determination of the above-named metals. For the details of this treatment with sulphuric acid, see p. 169.

A solution containing tartaric acid and ammonium hydrate may also be used to effect the separation of these metals, in place of the nitric acid solution. The E.M.F. required is practically the same as that named above.

The fact that mercury can be deposited in very satisfactory form from solutions containing an excess of potassium cyanide by means of almost any E.M.F. or current density has already been noted ; and the solution of the double cyanide salt may also be used to effect the separation of mercury from the metals named above.

The 'decomposition value' of the double cyanide salt of mercury and potassium is equivalent to about 1.60 volts ; and the E.M.F. of the current used to effect the separation may be allowed to rise to 2.50 volts without any of the other metals named being deposited with the mercury at the kathode.

If from 2 to 3 grms. pure potassium cyanide be added to the neutral solution of the mixed salts, a current of .08 ampère density can be obtained from the above E.M.F. The solution is heated to 50° or 60° C. before electrolysis, and the time required to deposit .50 gm. mercury is between five and six hours.

When cobalt is present the time required to deposit the mercury is increased. When using the double cyanide solution for the separation of mercury and cadmium it is necessary to keep the E.M.F. used for the electrolysis at from 1.80 to 1.90 volts, and in this case the deposition of the mercury is conveniently carried out at night. The separation from cadmium in an acid solution demands, however, less time and attention.

Mercury may also be separated from aluminium, magnesium, and the alkali metals in acid or cyanide solutions by use of any E.M.F., or current density, that may be thought suitable by the experimenter.

GOLD

Gold from Silver.—See p. 191.

Gold from Mercury.—See p. 195.

Gold may be deposited from a hydrochloric acid solution by means of a current with an E.M.F. of only one volt, but the deposit so obtained is not very adherent, and it is much the better plan always to make use of the double cyanide solution. This on electrolysis yields an even and bright coating of the metal upon the kathode surface.

The 'decomposition value' of the double cyanide of gold and potassium is somewhat higher than those of the corresponding salts of silver and mercury. In such a solution the separation of gold from zinc, copper, nickel, cobalt, and iron may be effected by means of a current the E.M.F. of which does not exceed 2·5 volts.

If the amount of each metal present be about ·10 gm., and if from 1·0 to 2·0 grms. pure potassium cyanide have been used in preparing the solution, a current density of between ·05 and ·10 ampère may be used. According to Smith and Wallace,¹ from three to three and a half hours will be requisite to complete the deposition. If a lower current density be used, it is perfectly feasible and safe to allow the electrolysis to continue through the night.

Smith and Muhr² state that gold may also be separated from palladium, platinum, and osmium by this method. In this case, from 2 to $2\frac{1}{2}$ grms. potassium cyanide are used with a current density of about ·05 ampère, and the time required is between twelve and fourteen hours.

Gold can also be deposited from a sodium sulphide solution, and this fact renders it possible to effect a separation by electrolysis of gold and arsenic.

A similar method cannot be applied to effect the separation of gold from antimony and tin. It was hoped that as gold cannot be deposited from an ammonium sulphide

¹ *Jour. Amer. Chem. Soc.* 1895, 17, 612.

² *Berichte*, 1891, 2171.

solution, a separation from tin would be effected by electrolysis of such solutions ; the experiments, however, did not yield successful results. Arsenic may not only be separated from gold in the sulpho-salt solution described above, but such a separation is also possible in the double cyanide solution.

The separation of gold and antimony may be effected by adding from .50 to 1.0 grm. tartaric acid, and then excess of potassium cyanide to the solution of the mixed metal salts. The antimony remains in solution when this mixture is electrolysed, and the gold deposit is obtained perfectly free from antimony.

PLATINUM

Platinum from Silver.—See p. 192.

Platinum from Mercury.—See p. 196.

Platinum from Gold.—See p. 198.

The electrolysis of chloroplatinic acid can be effected with an E.M.F. of only 1.1 volts, but this compound requires for its complete decomposition at least 1.5 volts. Since the solutions of mercury, gold, copper, and antimony containing hydrochloric acid require an E.M.F. of only 1.6 volts to produce electrolytic decomposition, this method is not adapted for separating platinum from these metals. In the case of arsenic and tin the separation is possible, but even for these metals it is not completely satisfactory. The separation of platinum from arsenic can be effected by means of the same E.M.F. in a sulphuric acid solution.

Platinum may be separated from the metals nickel, cobalt, iron, cadmium, and zinc, in any acid solution, by means of a current the E.M.F. of which lies between 1.8 and 2.0 volts, and the current density between .07 and .08 ampère.

In solutions containing excess of potassium cyanide, the platinum is so strongly held in combination that the separation from silver, gold, and mercury is easily effected. The platinum remains in solution, while the other metals are

deposited. These separations are described under the headings of the various metals. (See above.)

BISMUTH

Bismuth from Copper.—See p. 185.

Bismuth from Lead.—See p. 188.

Bismuth from Silver.—See p. 191.

Bismuth from Mercury.—See p. 194.

Bismuth can be deposited from either nitric or sulphuric acid solutions, and it follows from this that it may be electrolytically separated from iron, nickel, cobalt, zinc, and cadmium. These separations, however, suffer from the disadvantages noted under 'Bismuth.' The deficiencies of the direct method of deposition of this metal may, however, be overcome by adding a weighed amount of a mercury salt to the solution of the salts of the two metals whose separation is required. The bismuth is then obtained as an amalgam at the cathode ; and a complete separation from the other metals is possible if the conditions noted as requisite for the separation of mercury from nickel, cobalt, iron, zinc, and cadmium are maintained during the electrolysis (see p. 196).

Bismuth may be separated from arsenic, but not from antimony, by use of an E.M.F. of 1.9 volts with a sulphuric acid solution.

ANTIMONY

Antimony from Copper.—See p. 186.

Antimony from Silver.—See p. 191.

Antimony from Mercury.—See p. 194.

Antimony from Gold.—See p. 199.

Antimony from Arsenic.—These two metals behave alike in alkaline or hydrochloric acid solutions, when present in the lower state of oxidation. If, however, both are present in forms equivalent to the pentoxide, the antimony alone can be electrolytically deposited. This method for separating these two metals is, however, not

practicable with hydrochloric acid solutions, as the antimony deposited possesses many unsatisfactory characteristics. The best solution to use for effecting this separation is that of the sulpho-salts prepared by use of excess of sodium sulphide. In order to carry out such an electrolytic separation of arsenic and antimony, 1 grm. each of tartar-emetic and of sodium arsenate are dissolved in water, and to the solution 1 to 2 grms. sodium hydrate and 50 c.cms. of a saturated solution of sodium sulphide are added. The mixture is diluted to 150 c.cms. heated to between 50° and 70° C., and electrolysed with a current of from 1·0 to 1·5 ampères in density. The E.M.F. required will lie between 1·7 and 2·0 volts ; the time will be from one and a half to two hours. If it be desired to use currents of from ·30 to ·40 ampère in density, and to allow the electrolysis to run during the night, it is necessary to direct attention to the irregularities that may arise from the formation of polysulphides. When using this method antimony is obtained as a silvery grey deposit, while arsenic remains in solution. In order to determine the latter, the solution remaining after deposition of all the antimony is decomposed with sulphuric acid, the precipitate of arsenic pentasulphide and sulphur is treated with hydrochloric acid and potassium chlorate, and the arsenic determined by the gravimetric method as the ammonium and magnesium salt. The above method for effecting separations of antimony from arsenic is frequently used in technical laboratories, in place of the inconvenient and troublesome gravimetric method of analysis.

Antimony from Tin.—While antimony is easily deposited from a concentrated sodium monosulphide solution, tin cannot be separated from such a solution by electrolysis until it has been strongly diluted, and upon this difference a method of separation has been based. In order to carry out such an electrolysis, 1 grm. tartar-emetic and ·50 grm. stannous chloride, or in its place 1 grm. of the double chloride of tin and ammonium, are dissolved in water, and to this solution 1 to 2 grms. sodium hydrate and

50 c.cms. of a cold saturated solution of sodium monosulphide are added. The mixture after dilution to the usual volume is heated to the boiling point or at least to 60° to 70° C., and is electrolysed at this temperature with a strong current of from 1.0 to 1.5 ampères density. The E.M.F. required will lie between .90 and 1.7 volts, and to separate the antimony contained in 1 gm. tartar-emetic from one and a half to two hours will be demanded. The deposit will be bright and steel grey in colour, and it will be found best to employ a roughened electrode as kathode. Using currents of 1.0 ampère it is possible to deposit .16 to .20 gm. antimony per hour from such solutions, and this fact is important, because by its aid one can approximately calculate the duration of the electrolysis.

This must not be allowed to continue longer than is required for the complete deposition of the antimony, since long-continued electrolysis of these solutions produces polysulphides, and from solutions containing these tin may be deposited with the antimony.¹ For this reason it is not advisable to attempt this separation at the normal temperature by means of feeble currents during the night; under such conditions one is almost certain to obtain a deposit of antimony containing tin. The method first described, in which a strong current and a high temperature are employed, has, on the other hand, been frequently used in technical laboratories, and has been found to give absolutely correct results. If these are not attained by others, the failure can only be ascribed to their non-observance of some of the requisite conditions. The remarks made under 'Antimony' concerning the preparation of the sodium sulphide, the treatment of the deposit, &c., apply in this case also (see p. 145) If one has made use of a platinum basin electrode for

¹ When tin is present in very small amounts only, the separation of antimony and tin by means of strong currents is sufficiently accurate for practical purposes. When the tin is present in larger amount it deposits with the antimony if currents over .30 ampère in density be used, since the E.M.F. of such currents will exceed that required to decompose the tin sulphide—namely, 1.20 to 1.30 volts.

receiving the deposit of antimony, it is necessary to displace the remaining electrolyte by water before breaking the circuit. This electrolyte, freed from antimony, cannot be used directly, however, for the determination of the tin. It is first requisite to reduce it by evaporation to a volume of about 150 c.cms., and to convert the sodium sulphide into ammonium sulphide by the aid of 25 to 30 grms. ammonium sulphate and fifteen to thirty minutes' boiling. The end of this reaction is indicated by the brown colour that the liquid assumes, and by its smell. When it is completed, the solution is made up to the usual volume, and the deposition of the tin effected at a temperature of 70° C., with a current of from 1.0 to 2.0 ampères in density. The E.M.F. required will be from 3.3 to 4.0 volts, and the time about one hour.

From this solution between .30 and .40 gram. tin can be deposited per hour by means of a current of one ampère.

The deposition of the tin may also be undertaken at the normal temperature instead of at 70° C. The deposit is bright and of a greyish colour; its further treatment has already been described under 'Tin' (see p. 151). In carrying out this separation, if the instructions given above relative to the amount and the degree of concentration of the sodium sulphide solution have been exactly followed, the electrolysis of the solution will yield a yellow deposit at the anode composed of sulphur alone; if, however, too little sodium sulphide has been employed, both antimony and tin sulphides will be deposited with the sulphur at the anode, and these will, in most cases, not pass into solution again during the electrolysis. If, instead of the salts named above, a mixture of the two sulphides of antimony and tin similar to that obtained in the ordinary course of analysis be used, the preparation of the solution and its electrolysis are carried out exactly as described above. An alteration in the method is only called for should the precipitate of the mixed sulphides be suspected to contain much free sulphur.

If this were the case, a sodium polysulphide solution would be formed, and the separation of the antimony would be incomplete. A similar solution is formed when substances containing antimony and tin are opened up by fusion with dehydrated sodium hyposulphite, or with soda and sulphur.

In these cases the solution containing the polysulphides is treated with excess of an ammoniacal solution of hydrogen peroxide, and is warmed. The sulphur is oxidised, and the solution becomes colourless.

The resulting liquid is evaporated to a small volume, 50 c.cms. sodium monosulphide is again added, and the separation of the antimony and tin is carried out as already described.

The electrolytic method for effecting the separation of antimony and tin excels the ordinary analytical methods of separation for these two metals in both simplicity and speed. On this account the method has been very widely made use of in technical and analytical laboratories.¹

CADMIUM

Cadmium belongs to that group of metals the 'decomposing values' of whose salts lie above those of the corresponding salts of hydrogen or acids.

It occupies, however, a distinct place in this group, since, unlike iron, cobalt, nickel, and zinc, it may be deposited from a solution containing a small amount of free sulphuric acid. It is also much more easily deposited from the double cyanide solution than the other metals of the group. The behaviour of this metal on electrolysis finds an analogy in its behaviour towards sulphuretted hydrogen.

The separation of cadmium from those metals which can be deposited in acid solutions is most satisfactorily undertaken with nitric acid solutions. The separation of cadmium from the metals iron, cobalt, nickel, zinc, is more difficult.

¹ [Waller states in *Zeits. f. Electrochem.* 4, 247, that if an E.M.F. of .70 volt be exceeded, Tin will be deposited with the Antimony.—*Translator's note.*]

Cadmium from Copper.—See p. 174.

Cadmium from Lead.—See p. 190.

Cadmium from Silver.—See p. 192.

Cadmium from Mercury.—See p. 196.

Cadmium from Zinc.—The separation of cadmium from zinc, a metal to which it is closely allied, is possible in the solution of the double cyanides.

In order to carry out such a separation, the neutral solution of the sulphates of the two metals is treated with between 4 and 5 grms. pure potassium cyanide, diluted to about 150 c.cms., and electrolysed with a current the E.M.F. of which, according to Freudenberg¹ and Smith and Frankel,² must not exceed 2·6 volts. The deposition of the cadmium occurs exceedingly slowly, and eighteen to twenty hours are requisite for ·30 gm. of the metal. The deposit exhibits the silvery white colour of the metal.

The zinc remains in solution under the current conditions named, but by use of a stronger current it may be deposited directly from the same solution upon a new kathode. One may also convert the double cyanide of zinc salt into some other form suited for the deposition of this metal, but the first method is the simpler.

Since cadmium can be deposited from a solution which is slightly acidified with sulphuric acid, while the deposition of zinc from such a solution is impossible, this form of solution may also be used to effect the separation of these two metals.

The solution of the two salts is treated with 3 to 4 c.cms. of a concentrated ammonium sulphate solution and 2 to 3 c.cms. dilute sulphuric acid. The mixed solutions are then diluted to 150 c.cms., and the electrolysis is conducted with a current of ·08 ampère density under an E.M.F. of between 2·8 and 2·9 volts. The separation is complete; the cyanide method is, however, to be preferred, since the

¹ *Zeitschr. f. phys. Chem.* 12, 116.

² *Amer. Chem. Jour.* 3, 385.

deposit of cadmium obtained from a sulphuric acid solution is not always metallic in character.

A solution containing a small quantity of free acetic acid may be used in place of the sulphuric acid solution. In order to prepare such a solution, the acetates or sulphates of the two metals are dissolved in water, 3 grms. sodium acetate is added, and the liquid is acidified by means of a few drops of acetic acid. After dilution of this solution to 150 c.cms. it is heated to 70° C., and electrolysed with a current the E.M.F. of which is 2·2 volts. According to Yver,¹ from three to four hours are required to deposit ·20 gm. cadmium. The deposit obtained is crystalline in structure. Eliasberg states that a separation of these two metals may be obtained by use of the double oxalate solution.² In order to prepare this, the neutral solution of the two salts is treated with 8 to 10 grms. potassium oxalate and 2 grms. ammonium oxalate, and is then diluted to the usual volume. The electrolysis is carried out with this solution after warming, by means of a current of ·01 ampère density ; from six to seven hours will be required to deposit ·20 gm. cadmium.

The zinc may then be deposited from the same solution by means of a stronger current.

The solutions prepared for electrolysis with sodium phosphate and free phosphoric acid have also been recommended by Smith for use in effecting the separation of cadmium and zinc.³

Smith and Knerr have also shown that the solution prepared by adding 3 to 4 grms. sodium tartrate and some free tartaric acid to the neutral solution of the two salts yields on electrolysis, by means of a current of ·30 ampère density, a deposit of cadmium free from zinc.⁴

Cadmium from Nickel and Cobalt.—The separation of

¹ *Bull. de la Soc. Chem.* **34**, 18 ; *Zeitschr. f. anal. Chem.* **20**, 1881, 417.

² *Zeitschr. f. anal. Chem.* **24**, 548.

³ *Amer. Chem. Jour.* **12**, 329 ; **13**, 206.

⁴ *Ibid.* **8**, 200.

cadmium from these two metals can be effected in a solution slightly acidified with sulphuric acid.

The solution of the mixed salts is treated, as in the case of the separation of cadmium from zinc, with ammonium sulphate and a little free sulphuric acid, and is electrolysed with a current the E.M.F. of which does not exceed 2·8 or 2·9 volts. The deposit of cadmium obtained from this solution is completely free from nickel or cobalt. The remarks made under the separation 'Cadmium-Zinc' concerning the character of the deposit obtained from the sulphuric acid solution apply in this case also.

The double cyanide method described under Cadmium-Zinc may also be used to separate cadmium from cobalt. The neutral solution of the mixed salts is treated with 4 to 5 grms. pure potassium cyanide, and is electrolysed with a weak current, the E.M.F. of which, according to Smith and Frankel¹ and Freudenberg,² must not exceed 2·6 volts. These authorities state that this method is not applicable to the separation of nickel and cadmium. Smith and Wallace, however, have found that if 2 grms. sodium hydrate be added to the cyanide solution, and if the electrolysis be allowed to proceed during the night, using a current of ·20 ampère density, a deposit of cadmium completely free from nickel can be obtained.³

Solutions containing phosphates and a small amount of free phosphoric acid have also been proposed for effecting the separation of cadmium from nickel and cobalt.

Cadmium from Iron.—These metals may be completely separated by means of electrolysis in a solution containing ammonium sulphate and free sulphuric acid, similar to that recommended for effecting the separation of cadmium from zinc, nickel, and cobalt. The E.M.F. of the current employed must not exceed 2·8 volts. The deposit of cadmium obtained as in the previous separation is not

¹ *Amer. Chem. Jour.* **12**, 104.

² *Zeitschr. f. phys. Chem.* **12**, 116.

³ *Jour. anal. u. appl. Chem.* **6**, 87.

always satisfactory in character. The separation of these two metals may also be effected in a phosphate solution.

Cadmium from Manganese.—The latter metal is deposited from a sulphuric acid solution as peroxide at the anode, whereas cadmium, as already noted, may be deposited from such a solution if the amount of free acid present is not too great. A separation of these two metals is therefore possible. The amount of the metals present in the electrolyte must be small.

The larger electrode is used as anode, and it is preferable to use one with a roughened surface for this purpose. The solution is prepared as already described under Cadmium-Zinc.

Cadmium from Aluminium, Chromium, Magnesium, Calcium, Barium, Strontium, Potassium, and Sodium.—The separation of cadmium from these metals is easily effected either in solutions slightly acidified with sulphuric acid, or in those containing an excess of potassium cyanide. No deposition of the other metals occurs.

Cadmium from Arsenic, Antimony, and Tin.—In a solution containing cadmium and arsenic, the separation of the two metals may be effected by raising the arsenic to the arsenic acid stage of oxidation, adding 2 to 3 grms. potassium cyanide to the neutral solution, and electrolysing with a weak current. According to Freudenberg, and Smith and Frankel,¹ the separation is complete if the E.M.F. be not allowed to exceed 2.6 volts ; but the time required is great—namely, ten hours. Cadmium may also be separated from arsenic, antimony, and tin by use of an ammoniacal solution containing tartaric acid, if these metals be present in the higher state of oxidation. The cadmium obtained, however, from this solution is not in a form adapted for weighing.

Cadmium from Wolfram, Molybdenum, Osmium.—Smith states that cadmium may be separated from these metals in solutions containing an excess of potassium cyanide.

¹ *Amer. Chem. Jour.* 12, 428.

IRON

The methods by which this metal can be separated from those which are deposited in acid solutions have already received notice under the concerned metals. As a general rule, solutions strongly acidified with the mineral acids are used.

The separation of iron from the group of similar metals—cobalt, nickel, and zinc—offers on the contrary considerable difficulty, since in order to obtain deposits free from carbon and exact results, practically only one form of solution is available—namely, that containing ammonium oxalate. Solutions containing tartaric or citric acid cannot be used.

Iron from Copper.—See p. 169.

Iron from Lead.—See p. 190.

Iron from Silver.—See p. 192.

Iron from Mercury.—See p. 196.

Iron from Cadmium.—See p. 207.

Iron from Gold.—See p. 198.

Iron from Bismuth.—See p. 200.

Iron from Cobalt and Nickel.—The attempts made to separate these metals in solutions of their double oxalate salts failed on account of the fact that the ‘decomposition values’ of these salts lie very closely one to the other. Classen has, however, published a method by which this difficulty is overcome.¹ To the solution of the mixed salts of nickel and iron, 8 grms. ammonium oxalate are added, and after dilution the solution is electrolysed at a temperature of 60° or 70° C., with a current of between 1 and 2 ampères density. The E.M.F. required will be from 3 to 4 volts, and the time between two and three hours, for 30 grm. of the metals. If a weaker current be used, it is necessary to increase it to at least 1 ampère in density towards the end of the electrolysis, in order to remove the last traces of the metals from the electrolyte. The deposit

¹ Electrolyse.

obtained at the kathode is a bright and steel-grey alloy of iron and nickel. It is washed and dried as described under these metals. After weighing, the deposited alloy is brought into solution by warming with sulphuric or hydrochloric acid. The alloy is not easily soluble, and the acids must not be used too dilute. In any case considerable time will be required. The iron is present in this solution in the ferrous state, and its estimation is effected by titration with potassium permanganate. Owing to the green tint of the acid solution of the alloy of iron and nickel, the end of the reaction with the permanganate is obscured, and an addition of a solution of cobalt sulphate is made previous to the titration in order to overcome this difficulty.

This addition in some cases produces the desired result, and a colourless solution is obtained for the permanganate titration ; but it is not always effectual, and the results obtained in these cases are inexact. The separation of iron from cobalt may be carried out in a similar manner. An addition of nickel sulphate is used here to neutralise the pink colour of the solution. The results obtained are similar to those with nickel and iron.

Vortmann has proposed another method for separating iron from nickel and cobalt. The iron in the solution of the mixed salts is oxidised by means of bromine, and 6 to 8 grms. ammonium sulphate and a slight excess of ammonium hydrate are then added. A flocculent precipitate of ferric hydrate is produced ; this remains suspended in the solution. The nickel or cobalt is then deposited by means of a current of from .40 to .80 ampère in density. This deposit always contains a small amount of iron, which is removed by dissolving the deposit, and redepositing it from the comparatively pure solution thus obtained. This double deposition makes the method a troublesome one, and, apart from this, no method can be recommended in which one of the substances in the electrolyte is present as a flocculent precipitate during the electrolysis.

No simple and rapid electrolytic method for the separa-

tion of iron from cobalt and nickel exists. There is further little need for such, since the quantitative separation of these metals is easily effected by chemical methods.

Iron from Zinc.—This separation cannot be effected in solutions of the double oxalate salts for the same reason as that given under 'Iron-Nickel.' Classen has therefore recommended the deposition of these two metals as an alloy, under similar conditions to those given above, and after weighing the alloy, the determination of the iron by titration with permanganate.¹

In this case there is no difficulty arising from the colour of the iron-zinc solution ; but the simultaneous deposition of the two metals is not without some objectionable features. If a double oxalate solution, in which the two metals are present in about equal amounts, be electrolysed, more of the zinc than of the iron will be deposited at first. As the electrolysis proceeds, a portion of the zinc deposited will pass into solution again, and an evolution of gas will occur. The deposition of the alloy only takes place satisfactorily when the amount of zinc present is less than one-third that of the iron.

Vortmann has recommended the use of a solution containing a sufficient excess of potassium cyanide to hold the cyanides of the metals in solution, and sodium hydrate.² This latter forms sodium ferrocyanide with the iron, and this salt is not decomposed by the current in presence of free alkalies. Too great an excess of potassium cyanide delays the deposition of the zinc.

A current density of from .30 to .60 ampère is employed. As regards the practical utility of this method, the remarks under 'Iron-Nickel' apply here.

Iron from Manganese.—A great number of experiments have been carried out with all forms of salts, in order to discover a reliable method for obtaining a complete separation of these two metals, but without success. In

¹ Electrolyse.

² *Monats. f. Chem.* 14, 536.

most of these experiments the aim has been to obtain the manganese as peroxide at the anode, or to keep it in solution while the iron is deposited at the kathode. The results obtained showed that the deposition of the iron was incomplete (at least for the first deposition), and that when the manganese was separated as peroxide this latter contained iron.

This difficulty arises in connection with the method proposed by Classen.¹ The solution of the two metals is prepared by treating it with 6 or 8 grms. ammonium oxalate, and after heating to 50° or 60° C., the electrolysis is conducted with a current of 1 ampère in density, and of 3.1 to 3.8 volts as regards E.M.F. Only a small portion of the manganese is obtained at the anode as peroxide under these conditions. If less ammonium oxalate be used, permanganic acid and its salts will be formed at first at the anode, and later a peroxide deposit will be obtained containing iron. As a rule the liquid is rendered completely turbid by a brown flocculent precipitate, which partly settles in adherent form upon the kathode. The method gives inexact results in spite of all assertions to the contrary.

The method proposed by Brand,² in which a solution containing sodium pyrophosphate and ammonium oxalate is used, also yields inaccurate results.

If one attempt to effect the separation of iron from manganese in a solution containing 20 to 30 grms. ammonium acetate, an incomplete deposition of the manganese as peroxide occurs, owing to the formation of a ferrous salt which dissolves the peroxide again at the anode. Engels has proposed to add oxidising agents in order to overcome this difficulty.³ If chromic acid be used to oxidise the ferrous salt, a complete deposition of the manganese as peroxide can be obtained, but the deposit will be found to contain up to .02 gm. iron, probably in the form of oxide.

¹ Electrolyse.

² *Zeitschr. f. anal. Chem.* **28**, 581.

³ *Zeitschr. f. Elektrochem.* **2**, 414.

Iron from Aluminium.—If a solution of an iron salt containing alum be treated with 8 grms. ammonium oxalate and be then electrolysed, a deposit of iron alone will be obtained at the kathode at the commencement of the electrolysis. As aluminium can in no case be deposited from an aqueous solution, the separation is complete. In course of the electrolysis of solutions containing ammonium oxalate, carbonic acid is formed at the anode.

This leads to the formation of ammonium carbonate in the electrolyte, and to the precipitation by the latter of aluminium as a flocculent hydroxide.

The separation of aluminium hydrate does not produce any impurity in the deposit of iron. The electrolysis is conducted at the normal temperature, with a current that does not exceed 1 ampère in density. Stronger currents than 1 ampère heat the electrolyte and accelerate the formation of ammonium carbonate.

The E.M.F. required will lie between 3 and 3·8 volts, and about four hours will be demanded for the deposition of ·10 gm. iron.

As a rule a smooth deposit of iron is obtained, but towards the end of the electrolysis the aluminium hydroxide has a tendency to adhere to the deposit on the kathode.

When this has occurred, it may be removed without injury to the coating of iron by wiping with a cloth. The aluminium must be estimated by gravimetric methods.

If it be thought necessary to avoid the separation of the aluminium as hydroxide in the electrolyte, the solution containing the iron salt and the alum is treated with 1 gm. potassium tartrate, and after heating to 50° or 60° C. is electrolysed with a current of about 1 ampère in density. The E.M.F. required will be from 4 to 5 volts, and about five and a half hours will be requisite for ·10 gm. iron.

This solution will remain clear to the end of the electrolysis. A bright deposit of iron will be obtained, but it will be found to contain some carbon. The amount of this latter impurity does not exceed 1 mg. for the above-

named weight of potassium tartrate, so that the results obtained are only slightly erroneous.

Iron from Chromium.—A solution of either a ferric or ferrous salt containing any soluble salt of chromium sesquioxide may be prepared for electrolysis by adding 8 grms. ammonium oxalate.

The solution is then heated to 60° C., and is electrolysed by means of a current of from 1 to 2 ampères in density. The E.M.F. required will be from 3·3 to 3·7 volts ; in order to deposit ·10 gm. iron from three to four hours will be necessary. The deposit obtained is bright and metallic. The chromium salt is raised to the chromic acid state of oxidation during the electrolysis, and the chromium is determined in this solution by gravimetric methods.

COBALT AND NICKEL

Since cobalt and nickel belong to the group of metals which as a general rule cannot be deposited in acid solutions by means of the electric current, the separation of these two metals from many of the others is easily accomplished. The methods in use have already been described under the headings of the different metals, and a few methods of separation from metals of the same group have also already received mention.

Cobalt and Nickel from Copper.—See p. 172.

Cobalt and Nickel from Silver.—See p. 192.

Cobalt and Nickel from Mercury.—See p. 196.

Cobalt and Nickel from Bismuth.—See p. 200.

Cobalt and Nickel from Lead.—See p. 190.

Cobalt and Nickel from Cadmium.—See p. 206.

Cobalt and Nickel from Iron.—See p. 209.

Cobalt from Nickel.—Vortmann has proposed two methods¹ for effecting the separation of these two metals, so closely allied in their general properties and characteristics. The first consists in the use of a solution of the neutral sulphates of the two metals to which sulphates of the

¹ *D. R. P. Kl.* 40, 78236. *Monatshefte f. Chemie.* 14, 548.

alkali or alkaline earth metals have been added, together with a soluble chloride salt. The solution is then electrolysed with a current, the direction of which is continually changed, oxidation and reduction alternately occur at the electrode, and the cobalt is said to separate as hydrate while the nickel remains in solution.

The method is unsuitable for the purpose of electrolytic analysis, since quantitative results cannot be expected with it. The other method depends upon the use of solutions containing tartrates of the alkali metals, and a little potassium iodide. The results obtained with this method are also unsatisfactory, and a reliable electrolytic procedure for the separation of cobalt and nickel does not therefore exist.

Cobalt and Nickel from Zinc.—There are two ways in which the separation of these metals can be effected. Either the nickel or the zinc may be deposited, while the second metal remains in solution. According to Vortmann, in order to deposit the zinc from such a mixture of salts, the solution, which should contain about .20 grm. each of the concerned metals, should be treated with 5 to 6 grms. sodium potassium tartrate and with an excess of sodium hydrate, and should then be diluted to a volume of 150 c.cms.¹ The electrolysis is conducted at the normal temperature with a current of from .30 to .60 ampère in density. From two and a half to three and a half hours will be required in order to deposit the whole of the zinc.

Nickel monoxide often separates at the anode during this electrolysis. Towards the end of the deposition of zinc it frequently happens that a flocculent precipitate of nickel hydrate separates in the electrolyte, and ultimately this hydrate may settle upon the zinc at the kathode in fine brown streaks. This, however, can only occur when the electrolysis has been permitted to continue for too lengthy a period of time. The most simple manner of determining whether the whole of the zinc has been deposited is to hang a narrow strip of brass over the edge of the basin electrode

¹ *Monatsch. f. Chemie*, 14, 536.

and to note whether any deposition of zinc occurs upon it. The solution remaining after the whole of the zinc has been removed is acidified with sulphuric acid, and, after addition of excess of ammonium hydrate, is made use of for the deposition of the nickel by the ammonium sulphate method described under 'Nickel.' The solution may also be treated with 25 c.cms. ammonium hydrate, and 15 to 20 grms. ammonium carbonate, and electrolysed at a temperature of 50° to 60° C., with a current of from $\cdot 80$ to $1\cdot 0$ ampère in density. From one to two hours will be required in order to deposit $\cdot 20$ gm. nickel.

A method of separation depending upon the deposition of the nickel has been proposed by von Foregger.¹

The electrolyte is prepared by treating the solutions of the two sulphates, which should contain about $\cdot 20$ gm. of each metal, with 10 grms. ammonium sulphate, 10 grms. ammonium carbonate, and 10 c.cms. strong ammonium hydrate. The mixed salt solution is then diluted to 150 c.cms., and is electrolysed at a temperature of 50° or 60° C., with a current which at first does not exceed $\cdot 30$ to $\cdot 50$ ampère in density, but which is later increased to a density of $1\cdot 0$ to $1\cdot 5$ ampères.

The nickel separates as an adherent deposit at the kathode, whereas the zinc remains in solution even at the higher current density.

It is striking that the deposit of nickel is sometimes of a brownish colour, due not to admixed zinc but to enclosed nickel sesquioxide.

This, when it occurs, renders the results too high. The electrolyte remaining after the separation of the nickel can be prepared for the electrolytic determination of the zinc by treating with an excess of sodium hydrate. The deposition of the zinc from this solution is then carried out at 60° or 70° C., with a current of from $\cdot 80$ to $1\cdot 0$ ampère in density. About three and a half hours will be required to deposit the zinc.

¹ *Dissertation*, Bern, 1896.

The methods of zinc deposition depending upon the use of the cyanide or oxalate double salts may also be used, if the necessary steps be taken to convert the zinc present in the solution that remains after deposition of the nickel, into these forms.

The two methods given above may also be used together; that is to say, the zinc is deposited according to the first, and the nickel in the remaining electrolyte is then deposited in accordance with the directions of the second.

Cobalt and Nickel from Manganese.—Classen has proposed to use a solution of the sulphate salts of these metals, to which about 8 grms. ammonium oxalate have been added, for effecting their separation.¹ The deposition of the nickel or cobalt is then effected similarly to that of iron from a corresponding solution, at a temperature of between 50° and 60° C., by means of a current of about 1·0 ampère in density. The E.M.F. required will be from 3·1 up to 3·6 volts. The cobalt or nickel separate at the kathode, whilst the deposition of the manganese is prevented by the ammonium oxalate present in the solution.

A formation of a dark-brown flocculent precipitate of manganese compounds occurs, however, and these settle upon and adhere to the metallic coating on the kathode. It is impossible wholly to avoid this precipitation, either by altering the temperature at which the electrolysis is carried out, or by varying the amount of ammonium oxalate used. The method is inexact.

Brand has proposed to separate cobalt from manganese in solutions containing sodium pyrophosphate,² but the method does not lead to successful results. Nickel may, however, be separated from manganese in such a solution if the amount of the two metals present is very small, and if the electrolyte contains in addition to the sodium salt 15 per cent. ammonium hydrate.

Neither of the two methods described for the separation

¹ Electrolyse.

² *Zeitschr. f. anal. Chem.* 28, 581.

of cobalt and nickel from manganese can be recommended as trustworthy.

Nickel and Cobalt from Aluminium and Chromium.—The separation of these metals is effected in the same way as that of iron from aluminium and chromium.

ZINC

Since zinc also belongs to that group of metals which are separated from their salts with greater difficulty than hydrogen is separated from its salts (the acids), it follows that the separation of zinc from many of the metals is easily accomplished. The methods used to effect such separations, and also other separations from the metals of the same group, have already received mention as follows :—

Zinc from Copper.—See p. 167.

Zinc from Lead.—See p. 190.

Zinc from Silver.—See p. 192.

Zinc from Mercury.—See p. 196.

Zinc from Gold.—See p. 198.

Zinc from Bismuth.—See p. 200.

Zinc from Cadmium.—See p. 205.

Zinc from Iron.—See p. 211.

Zinc from Cobalt and Nickel.—See p. 215.

Zinc from Manganese, Aluminium, and Chromium.—The methods described under iron and cobalt for the separation of these metals from manganese, aluminium, and chromium may also be used to effect the separation of zinc from the latter metals. The remarks concerning the trustworthiness of the methods also apply in the case of zinc.

MANGANESE

Manganese, which is nearly always deposited as peroxide, can be separated in acid solutions from a considerable number of the metals. These separations have already received full description, under the concerned

metals. The separation of manganese from those metals which cannot be deposited in acid solutions is attended by difficulties, and the results obtained in most cases are unsatisfactory.

These separations have likewise received mention under the individual metals.

SEPARATION OF SEVERAL METALS

If many metals be present in one solution, the methods of electrolytic separation employed are varied according to the electrolytic character of the metals present.

Magnesium, aluminium, chromium, calcium, barium, strontium, potassium, and sodium always remain in solution, as they cannot be deposited at the kathode under the ordinary current conditions.

The remaining metals can be easily separated into two large groups by electrolysing solutions containing a definite excess of certain acids.

In this way it may occur that many of the metals are deposited together ; a separation of the metals in such a composite deposit is only possible after redissolving.

For example, if a solution containing silver, copper, cadmium, and zinc be obtained for analysis, one would first deposit the silver and copper together, and then dissolve this mixed kathode deposit in order to effect the separation of the silver from the copper. If lead be present in such a mixed acid solution, the method of separation is also again very simple.

After electrolysis, those metals which can be deposited in the presence of free acid will be found at the kathode, the lead as peroxide at the anode, and the metals of the group Zinc-Iron will be found still in solution. In some cases, dependent upon the metals present, similar group separations are possible in solutions of the cyanides or other salts.

It is more advantageous, however, in practical analytic work, when dealing with solutions which contain several

metals, to separate these by purely chemical methods to such an extent, that either the electrolytic work is confined to depositions of single metals, or to separations for which definite data are available.

Examples of these combined chemical and electrolytic methods of analysis are given in Part III. D.

D. PRACTICAL EXAMPLES

Alloys of Copper and Zinc, containing Lead and Iron as Impurities (Brass, Tombac).—About 50 grm. of the sample obtained by boring or filing the alloy is dissolved, with the aid of gentle heat, in dilute nitric or sulphuric acid. The amount of acid requisite for the later electrolysis is 5 to 10 c.cms. strong nitric acid, or 3 to 5 c.cms. conc. sulphuric acid. The warm solution of the alloy is diluted to a volume of 150 c.cms., and is electrolysed either in a beaker with a cone electrode, or in the platinum basin, with a current of about 1 ampère in density, and under the conditions given in detail under Copper-Zinc on p. 167.

If the alloy under analysis be brass containing lead as an impurity, a nitric acid solution should be used with an anode that has been previously weighed. The lead separates upon the latter as peroxide; and as lead is only present in very small amounts in brass, the smaller electrode will in this case serve to receive it.

When the whole of the copper has been deposited (three to four hours will be requisite for this) the electrodes are removed from the electrolyte in the beaker, or the basin electrode is washed out before breaking the current circuit.

The remaining solution of zinc in nitric acid is treated with a small amount of sulphuric acid, and is evaporated in order to drive off the free and combined nitric acid. The sulphates of zinc and iron thus obtained are dissolved in a small quantity of water, and the latter is precipitated as

hydroxide, most simply by addition of a slight excess of ammonium hydrate to the aqueous solution of the sulphates.¹

This iron is then determined by the gravimetric method, or the hydroxide may be dissolved, and the iron determined electrolytically in an ammonium oxalate solution.

The sulphuric acid solution of zinc and iron that remains when the copper has been deposited from a sulphuric acid electrolyte is treated in the same manner in order to separate the iron. The slightly alkaline ammoniacal zinc solution obtained in either case is treated with a few grams of pure potassium cyanide, or with ammonium oxalate or lactate, according to one of the methods described under zinc on pp. 113–122, and the zinc is deposited as metal upon an electrode which has been previously coated with copper or silver. The preparation of the deposits of copper and zinc for weighing is, of course, carried out as already described in detail under these metals.

It is more convenient to precipitate the iron by means of ammonia, and to estimate it separately, than to electrolytically deposit zinc and iron together, and then to use the unsatisfactory electrolytic method for separation of these two metals.

Brass is composed as a rule of 65 per cent. copper and 35 per cent. zinc. Lead and iron are generally only present as impurities in very small amounts.

Alloys of Copper and Silver (Mint-Silver).—In order to carry out this analysis .20 to .60 grm. of the borings or filings of the alloy are dissolved in a small amount of nitric acid. This solution is then either directly used for the electrolytic separation of the silver and copper under the conditions described on p. 182, or it is neutralised with sodium hydrate, treated with excess of pure potassium cyanide, and electrolysed as described under this method on p. 183.

¹ [If much zinc be present, a larger excess of ammonium hydrate will be required to keep this metal in solution.—*Translator's note.*]

The German and United States mint-silver contains 90 per cent. of the metal ; that used in France varies from 83.5 per cent. up to 90 per cent. ; while there is 92.5 per cent. silver in the coinage-silver used at the mint in England.

Alloys of Copper and Nickel (Mint-Nickel).—The solution of this alloy for electrolysis is obtained by dissolving .30 to .50 gm. of the prepared sample in dilute nitric or sulphuric acid, and by adding in the former case still another 5 c.cms. conc. nitric acid. The deposition of the copper is then carried out under the current conditions detailed under Copper-Nickel (see p. 173). In order to determine the nickel in the remaining electrolyte, the nitric acid is removed by evaporation with an excess of sulphuric acid, and, after treatment with an excess of ammonium hydrate, the nickel is deposited directly from the resulting ammoniacal solution of sulphate salts. When sulphuric acid has been used to dissolve the alloy, more time is required to effect this, but the later evaporation with this acid is unnecessary ; and after deposition of the copper in the acid solution, one can simply add excess of ammonium hydrate, and proceed at once to deposit the nickel.

The details of the procedure will be found on p. 106.

If small amounts of iron be present as an impurity in the alloy, this will cause a precipitate of ferric-hydrate to form when the ammoniacal solution of nickel is being prepared for electrolysis.

This is removed from the solution by filtration, and the iron in it is determined either by the gravimetric method, or by redissolving and deposition from an ammonium oxalate solution.

The nickel coins used as currency in Germany contain 75 per cent. copper and 25 per cent. nickel.

Alloys of Copper, Zinc, and Nickel (German-Silver).—Three different methods may be employed to effect the electrolytic separation of the metals that occur in this

alloy. First, one may use a nitric acid solution, to deposit the copper alone, and then separate the nickel and zinc in the remaining electrolyte. Or, one can make use of an alkaline sodium potassium tartrate solution, and deposit the zinc and copper together as an alloy, while the nickel remains in solution to be later deposited alone.

The third method depends upon the use of an ammoniacal solution containing ammonium carbonate, from which on electrolysis copper and nickel are deposited as an alloy, zinc remaining in solution.

In order to carry out the first method, between .20 and .40 gram. of the alloy, preferably in the form of thin shavings, is dissolved in dilute nitric acid in a beaker. When the solution is complete, a further 20 to 30 c.cms. conc. nitric acid are added, the solution is diluted to 150 c.cms., and after cooling to the normal temperature it is electrolysed either in the beaker with a cone electrode, or in the platinum basin.

The density of current used should be from .50 to 1.0 ampère. The E.M.F. required will be from 2.5 to 2.8 volts, and the time from two to three hours. The remaining solution is then evaporated with sulphuric acid in order to remove the nitric acid and to convert the nitrates into sulphates, and after neutralising it is treated by either of the methods detailed on pp. 215, 216. In the one case zinc is first deposited; in the other, the nickel is determined first, and the zinc in the remaining electrolyte.

The second method is carried out as follows:—To the solution of .20 to .40 gram. of the alloy in nitric acid, after evaporation with sulphuric acid to convert the salts into sulphates, 6 grms. sodium potassium tartrate and 4 to 5 grms. sodium hydrate are added, and the mixture is then diluted to 150 c.cms. and heated to 40° or 50° C. The solution is then electrolysed with a current of .60 to .70 ampère in density. The whole of the copper and zinc will be deposited as an alloy in three to four hours. As the copper is deposited more rapidly than the zinc, the red

colour of the coating on the kathode will gradually pass into a grey. The mixed deposit after washing is dissolved in a few cubic centimetres of dilute nitric or sulphuric acid, and the separation of the copper and zinc in this solution is then undertaken as described under Copper-Zinc (see p. 168).

The current used should be about 1 ampère in density ; the time required will be from two to three hours.

The solution containing the nickel is treated with 15 grms. ammonium carbonate, and after heating to 30° to 50° C. is electrolysed with a current of between .80 and 1.0 ampère density. In from two to four hours the whole of the nickel will have been deposited as a bright metallic coating at the kathode.

In order to effect the separation of these three metals by the third method, between .20 to .40 gm. of the alloy is again dissolved in nitric acid and evaporated with sulphuric acid in order to convert the nitrates into sulphates. The solution is then treated with 10 grms. ammonium carbonate, 15 grms. ammonium sulphate, and 10 c.cms. ammonium hydrate. The solution diluted to the usual volume is heated to 50° C., and electrolysed with a current of .50 ampère density.

The deposition of the copper-nickel alloy demands from four to five hours, but if the electrolysis is allowed to continue for too lengthy a period of time, the deposit may become brown, owing to the formation of nickel oxides. This deposit is redissolved in sulphuric or nitric acid, and the nickel and copper are separated by the method described on p. 173. In order to effect the deposition of the zinc from the remaining electrolyte, one may add either excess of ammonium oxalate or of potassium cyanide to the solution, and electrolyse under the current conditions given under the descriptions of these methods on pp. 115 and 118. One may also prepare the solution for deposition of the zinc by evaporating off the greater part of the ammonia, and by adding 2 to 3 grms. sodium hydrate.

If the alloy should contain small amounts of iron as an

impurity, this will be precipitated on the addition of the ammonium hydrate or ammonium carbonate to the electrolyte. It is separated by filtration, and estimated either by the gravimetric method or by the electrolytic method in a double oxalate solution.

The composition of German silver varies between the following limits: copper, 50 to 66 per cent.; zinc, 19 to 31 per cent.; nickel, 10 to 18 per cent.

Alloys of Copper, Zinc, Nickel, and Silver (Old Swiss Nickel Coinage).—The earlier Swiss nickel coinage metal was a true alloy of copper, nickel, and zinc, with a little silver, whereas 'China silver' is merely 'German silver' coated with silver. In order to analyse this alloy by electrolytic methods one may proceed in two different ways. By the first method .20 to .40 grm. of the alloy, preferably in the form of filings, is dissolved in a small quantity of nitric acid, and after dilution the silver is precipitated as chloride by addition of a few drops of hydrochloric acid. The solution is then warmed, and, after filtering off the silver, is treated for the separation of the copper, nickel, and zinc by one of the methods just described under 'German Silver.' The silver in the separated silver chloride may either be determined in the usual gravimetric way, or the chloride may be dissolved in potassium cyanide solution, and the silver be deposited from this solution according to the conditions given under silver (see p. 136).

In the latter case the smaller electrode is used as kathode, on account of the small amount of silver present in the alloy.

The second method depends upon the deposition of the silver and copper as an alloy directly from the nitric acid solution in a manner similar to that described under 'German Silver.' The alloy is then redissolved and the two metals separated according to the method given on p. 182. It is better, however, to use at first a low E.M.F. and a feeble current, in order to obtain a deposit of the

silver alone ; afterwards the copper may be deposited by means of a stronger current. The remaining metals—nickel and zinc—may then be separated by the method given on p. 215.

Alloys of Copper and Tin (Bronze).—In order to prepare a solution of this alloy for electrolysis, .20 to .40 grm. of the extremely finely divided metal is dissolved in 6 c.cms. nitric acid of 1.5 sp. gr., and 3 c.cms. water are then added. When the first action has subsided, the solution is heated to boiling, 15 c.cms. boiling water are added, and the tin oxide is, after settling, filtered off, and washed. The filtrate contains all the copper, which may be deposited under the conditions given on p. 93, after the addition of a further 5 to 10 c.cms. nitric acid to the filtrate from the tin oxide. If the above instructions regarding the concentration of the nitric acid solution have been carefully carried out, the tin oxide which separates will be found free from copper ; this may not be the case if other proportions of acid and water have been used in bringing the alloy into solution.

The tin oxide collected on the filter may either be dried, ignited, and weighed ; or while still moist it may be dissolved in a solution of ammonium sulphide, and the resulting stannic sulphide solution electrolysed under the conditions given on p. 150.

The solution of the alloy may also be effected by means of aqua regia. In this case the solution is evaporated to dryness, and the residue is treated with a solution of sodium sulphide. The tin passes into solution, and the copper remains as insoluble copper sulphide. The latter is filtered off, and, after washing with water containing sulphuretted hydrogen, is dissolved in the necessary amount of nitric acid, and the copper determined electrolytically by the method given on p. 93. The solution of tin is boiled with ammonium sulphate in order to convert the sodium sulphide into the ammonium salt, and the tin is then deposited from this solution. Ammonium sulphide cannot be directly used in the treatment of the residue

from the aqua regia solution, since copper sulphide is slightly soluble in solutions of the polysulphides of ammonium.

The following are alloys of copper and tin :—Bronzes of the ancients ; cannon metal (9 to 10 per cent. tin) ; bell metal (20 to 25 per cent. tin) ; and speculum metal (30 to 35 per cent. tin).

Alloys of Copper, Tin, and Zinc (German Mint Copper, Modern Bronze).—In order to prepare a solution of this alloy for electrolysis .20 to .50 grm. of the alloy in a finely divided state is dissolved in nitric acid under the conditions as regards concentration of the solution mentioned under 'Bronze.' The tin oxide is filtered off, washed, and the tin determined either gravimetrically or by electrolytic deposition from an ammonium sulphide solution (see p. 150). The filtrate containing copper and zinc is then treated exactly as described on p. 168 for the separation of these two metals. If lead be present as an impurity in the bronze, it will be separated as peroxide at the anode during the deposition of the copper from the nitric acid solution, and it is estimated as usual from the weight of this peroxide deposit.

German mint copper contains 95 per cent. copper, 4 per cent. tin, and 1 per cent. zinc.

Alloys of Copper, Tin, Zinc, and Phosphorus (Phosphor Bronze).—If a finely divided sample of this alloy be treated with nitric acid as described under 'Bronze,' there will remain a residue of stannic phosphate which may be separated and weighed. Another sample of the alloy is treated in the same way, but the insoluble stannic phosphate is digested with sodium sulphide, and the solution containing the tin is then treated with ammonium sulphate and electrolysed as described on p. 150.

The difference between the weight of tin thus found and that of the stannic phosphate yields by calculation the weight of phosphorus contained in the alloy. The residue of copper and zinc sulphides remaining from the treatment with sodium sulphide solution is dissolved in nitric acid,

and these two metals are then separated by the method given on p. 168.

Alloys of Zinc and Tin (Counterfeit Silver-leaf).—A small portion of the alloy is dissolved in nitric acid under the conditions of solution described for 'Bronze,' and the tin is determined as there recommended. The nitric acid solution is freed from this acid by evaporation with sulphuric acid, and, after neutralising, the zinc sulphate solution is electrolysed as described under 'Zinc' (see p. 115).

Alloys of Copper and Aluminium (Aluminium Bronze).—The finely divided sample of the alloy is prepared for electrolysis by dissolving in nitric acid, and by addition of a further amount of nitric acid. This solution is then used for deposition of the copper as described on p. 93. The aluminium is determined by the gravimetric method in the remaining electrolyte. The alloy containing 3 per cent. copper is white, that containing 5 to 10 per cent. is golden yellow.

Alloys of Copper and Gold (Mint Gold).—A solution of this alloy is prepared by dissolving a small amount in aqua regia, and by evaporating the solution to dryness. The residue is treated with a small quantity of hydrochloric acid, and afterwards with sodium hydrate solution and with 2 grms. pure potassium cyanide. The gold is deposited from this solution first, under the current conditions given under 'Gold' (see p. 152), while the copper remains in solution, and is only deposited when a stronger current is employed.

German mint gold contains 90 per cent. gold, whereas that coined at the English mint contains 91·66 per cent. gold.

Alloys of Lead and Tin (Solder).—In order to prepare a solution of this alloy for electrolysis ·30 to ·50 grm. of the sample in small pieces is treated with a mixture of 6 c.cms. conc. nitric acid and 3 c.cms. water, and, when the first reaction is over, the whole is heated to a boiling temperature. The solution containing the tin as insoluble oxide is then diluted with 15 c.cms. water and filtered. The tin oxide is

washed, and the tin is determined either by direct weighing or by the electrolytic method described on p. 150. In the latter case the moist stannic oxide is dissolved in ammonium sulphide solution. The filtrate containing the lead as lead nitrate receives a further addition of nitric acid, and the lead is then determined electrolytically by deposition as peroxide in the manner described under 'Lead' (see p. 128).

Alloys of Lead, Tin, and Bismuth (Rose's Metal).—This alloy is prepared for electrolysis by treating the finely divided sample with nitric acid under the conditions described for 'Solder.' The tin oxide requires, however, in this case washing with water that contains nitric acid, in order to remove the basic bismuth nitrate that would otherwise remain with the tin on the filter. Since lead and bismuth cannot be separated by electrolytic methods in a nitric acid solution, it is necessary to evaporate the solution to a syrup consistency many times upon the water-bath, using water each time to bring the metal salts into solution.

When all the nitric acid has been driven off, a dilute solution of ammonium nitrate is added, and the insoluble basic nitrate salt of bismuth is filtered off. The filtrate after addition of nitric acid is used for deposition of the lead as peroxide. The tin is determined in the tin oxide as described under 'Bronze' (see p. 226). The bismuth nitrate precipitate may either be dried, ignited, and weighed as bismuth oxide, or dissolved, and the bismuth deposited as an amalgam in the manner described on p. 162.

Alloys of Tin, Lead, Bismuth, and Cadmium (Wood's Metal).—In order to analyse this alloy by electrolytic methods, the solution of the sample and determination of the tin and bismuth are carried out exactly as in the case of Rose's metal. The filtrate from the basic bismuth nitrate precipitate contains lead and cadmium, and, after addition of a sufficiency of nitric acid to keep the latter metal in solution, it is electrolysed.

The lead is obtained as peroxide at the anode.

The remaining electrolyte is treated according to one of the methods given under 'Cadmium' on p. 122, in order to determine this latter metal.

Alloys of Tin and Mercury (Tin Amalgam).—The alloy is prepared for electrolysis by dissolving a few decigrams in nitric acid, under the conditions of solution described for 'Solder.' The tin is determined as there noted; while the mercury may be directly deposited from the nitric acid solution by means of the current and E.M.F. mentioned on p. 140. The solution of the alloy may also be effected by the use of aqua regia at a gentle heat. The free chlorine is then driven off by further heating, and, after neutralising with ammonium hydrate, the solution is treated with ammonium chloride and ammonium sulphide solutions.

A precipitate of mercury sulphide is obtained which may be separated and redissolved, and the solution, after removal of the excess of free acid, used for deposition of the metal according to one of the methods given on p. 140. The solution of the tin sulpho-salt is used directly for the electrolytic determination of the tin.

Alloys of Lead and Antimony (Hard Lead, Type Metal).—These alloys contain as a rule, in addition to the lead, 18 to 25 per cent. antimony and small quantities of copper and iron. The simplest method of analysis is as follows: 2.5 grms. of the alloy are placed in a $\frac{1}{4}$ -litre flask with 10 grms. tartaric acid, 15 c.cms. water, and 4 c.cms. conc. nitric acid, and gently warmed. The clear solution is treated with 4 c.cms. conc. sulphuric acid, diluted, and after cooling the flask is filled up to the mark. 50 c.cms. of the filtrate, corresponding to .50 gm. of the alloy, are then made strongly alkaline with sodium hydrate solution, and are boiled with 50 c.cms. of a saturated sodium sulphide solution. The resulting liquid is at once filtered, and the filtrate while still hot electrolysed with a strong current, under the conditions given on p. 145, for the deposition of antimony. In order to determine the copper that may be

present, the residue that remains from the treatment with sodium sulphide solution is dissolved in nitric acid, the solution is diluted, filtered, and the copper deposited as described on p. 93. If it be thought necessary to determine the lead separately, .50 gm. may be used instead of 2.5 grms. of the alloy, and the lead sulphate precipitated by the addition of sulphuric acid, collected and weighed. It is better, however, to treat the solution of the metals directly with sodium hydrate and sodium sulphide.

The insoluble residue that remains after this treatment is made up of the sulphides of copper and lead. It is dissolved in nitric acid, and the separation of these two metals effected by the method described on p. 178.

The method first described excels the gravimetric method greatly in simplicity, and is very frequently used in technological laboratories for the analysis of this alloy.

Alloys of Antimony, Tin, and Arsenic (Britannia Metal).—The solution of this alloy is prepared for electrolysis by dissolving the sample in aqua regia, evaporating off the excess of acid, treating the residue with a small quantity of sodium hydrate solution, and then with 50 c.cms. of a saturated solution of sodium sulphide. All three metals pass into solution as sulpho-salts, but arsenic cannot be separated electrolytically from the solution, since it is present in the higher state of oxidation. The separation of the antimony is effected by the method given on p. 201 under 'Antimony-Tin.' If the electrolyte remaining after the deposition of the antimony be treated with hydrochloric or sulphuric acid, a precipitate of the sulphides of arsenic and tin mixed with sulphur is obtained. This is filtered off, and the arsenic sulphide separated by digestion with a solution of ammonium carbonate. The residue is then washed and dissolved in ammonium sulphide, from the solution in which the tin may be separated directly as described on p. 150.

The arsenic must be determined by gravimetric methods. It may either be precipitated, or distilled off from the

solution before the deposition of the antimony, or its determination may be left to the last. The former method is to be preferred. In either case the antimony is deposited from a sodium sulphide solution. This is then converted into an ammonium sulphide solution and electrolysed to obtain a deposition of the tin, according to the method described fully under 'Antimony-Tin' on p. 201.

The separation and determination of these three metals in the presence of each other by gravimetric methods is difficult and troublesome, and electrolysis proves itself in this case a very useful aid to the ordinary methods of analysis.

Refined Soft Lead.—The refined lead found in commerce always contains traces of other metals—silver, copper, bismuth, iron, nickel, zinc, tin, antimony, arsenic—which together make up some hundredths of 1 per cent.

It is customary in the analysis of this lead to estimate only the impurities. The analysis is conducted as follows : 200 grms. of the sample of lead cut into small pieces are put into a 2-litre flask, with 325 c.cms. nitric acid and 1275 c.cms. water. The solution of the lead is effected by the aid of gentle heat upon the sand-bath. To the clear solution 62 c.cms. conc. sulphuric acid are added, and, after cooling, the flask is filled up with water to the mark, and 1750 c.cms. of the liquid containing lead sulphate in suspension are filtered and evaporated to dryness in a porcelain basin. The residue is digested with water, and then brought upon a filter.

The insoluble residue (A) upon the filter is digested with 25 c.cms. of a saturated solution of sodium sulphide.

The filtrate (B) is acidified with hydrochloric acid, and sulphuretted hydrogen gas is then passed through it ; this separates it into a precipitate (C) and a filtrate (D). Precipitate (C) is digested with 25 c.cms. sodium sulphide solution. The digestion leads to the solution of the arsenic, antimony, and tin which may be contained in (C) ; the solution of the sulpho-salts obtained is added to that obtained earlier in the analysis. If a qualitative examina-

tion of the lead has shown that no arsenic is present, the antimony is deposited from this solution, and, after treatment with ammonium sulphate, the tin is deposited according to the method described on p. 150. If arsenic be present, the solution containing the sulphy-salts is decomposed with sulphuric acid, and the precipitate of the sulphides mixed with free sulphur is digested with a solution of ammonium carbonate for the removal of the arsenic. The antimony and tin sulphides that remain are then redissolved in sodium sulphide and separated as already described. The residue (c) is boiled with aqua regia, the silver chloride which separates is filtered off, and the silver either determined by the gravimetric method or by electrolysis of a potassium cyanide solution of this chloride. The former is the better plan.

The filtrate from the silver chloride is evaporated to dryness with a small quantity of sulphuric acid, in order to effect the separation of the remainder of the lead as sulphate; the residue is taken up with water, and the filtrate from the lead sulphate is neutralised with ammonia, and the bismuth precipitated by means of ammonium carbonate.

The bismuth is then electrolytically deposited as an amalgam according to the method given on p. 163. The ammoniacal filtrate from the insoluble basic bismuth compound contains the copper and cadmium. These metals are either separated by the method given on p. 175, or the solution is treated with 1 grm. pure potassium cyanide and with a small amount of sodium sulphide, whereby cadmium sulphide is precipitated. The cadmium sulphide is filtered off, dissolved in nitric acid, and, after evaporation of the solution with sulphuric acid, the cadmium is determined electrolytically by one of the methods given on pp. 122-126.

The copper contained in the cyanide solution may either be deposited directly, or after treatment with sulphuric acid, under the current conditions given on pp. 96-99.

The filtrate (D) from the precipitate with sulphuretted hydrogen is boiled to drive off the excess of gas, and, after oxidation by means of bromine water, is treated with an excess of sodium hydrate solution. The zinc passes into solution and is deposited either directly from this, or from some other salt solution obtained by chemical means from the sodium zincate solution. The precipitate of hydroxides produced by the addition of sodium hydrate to the filtrate (D) is dissolved in dilute sulphuric acid, the iron is precipitated with ammonium hydrate, and is determined either by the volumetric or the electrolytic method. The gravimetric method cannot be used, as the aluminium always present in sodium hydrate would be weighed with the iron oxide, and would cause an error in the results. The remaining solution containing nickel and cobalt is treated with ammonia hydrate, and these metals electrolytically determined by the method given on p. 106. The results obtained are calculated upon 179.12 grms. lead, since the volume of the lead sulphate produced in the measuring flask has to be allowed for.

Raw Lead, Argentiferous Lead.—This grade of lead contains from 1 to 4 per cent. of impurities. According to the degree of purity from 10 to 50 grms. of the sample are dissolved in nitric acid and water.

For every 10 grms. of lead 60 c.cms. water and 16 c.cms. nitric acid should be employed. The antimony present is kept in solution by aid of 5 to 10 grms. tartaric acid. In order to precipitate the lead as sulphate, 3 c.cms. conc. sulphuric acid are used for each 10 grms. lead dissolved, and 2.15 c.cms. are deducted as the volume of the lead sulphate produced. On account of the presence of tartaric acid the filtrate from the lead sulphate is not evaporated quite to dryness, and the treatment with sodium hydrate and sodium sulphide follows at once.

The remainder of the analytical procedure is conducted as already described under 'Soft Lead.'

Commercial Zinc.—The zinc of commerce always con-

tains, in addition to lead, small amounts of iron, cadmium, arsenic, antimony, tin, and copper. In order to determine these impurities it is necessary to dissolve from 20 to 100 grms. of the metal, according to its degree of purity. The weighed sample in the form of borings or small pieces is placed in an Erlenmeyer flask provided with a funnel tube and a gas-delivery tube, and, after the addition of warm water and dilute sulphuric acid, the solution of the zinc is effected at a gentle heat.

The gas that is given off on solution is passed through hydrochloric acid containing bromine, or through a solution of hydrogen peroxide in order to absorb the arseniuretted hydrogen that it may contain. Since zinc is a strongly positive metal, and separates all other metals from their salt solutions, all the metals present in the zinc as impurities will appear in the flask as a metal sponge, which will not be attacked by the acid until all the zinc has passed into solution. This spongy precipitate is therefore filtered off before the last traces of the zinc have dissolved. It will contain all the metals named as impurities of commercial zinc with the exception of the arsenic, which will be found in the absorbing solution through which the evolved gas was passed. The arsenic is separated by evaporating the solution, and by precipitating with sulphuretted hydrogen gas. The mass of spongy metal is dissolved in aqua regia, and, after evaporating off the nitric acid, sulphuretted hydrogen gas is conducted through the hydrochloric acid solution of the metals. The precipitate is digested with sodium sulphide, the solution of the antimony and tin sulpho-salts and the insoluble residue, which may contain lead, copper, cadmium, and bismuth, being treated further as already described under 'Antimony-Tin' (see p. 201) and 'Refined Soft Lead' (see p. 232) respectively.

The filtrate from the sulphuretted hydrogen precipitate may contain iron, zinc, and possibly manganese.

These are separated as described under 'Refined Soft Lead.'

It is advisable to test the solution of the zinc in excess of sodium hydrate, for iron, by means of a few drops of permanganate.

The arsenic, antimony, and tin may also be determined in a special sample of the zinc by dissolving in aqua regia, evaporating to dryness, taking up with hydrochloric acid, precipitating with sulphuretted hydrogen gas, and digesting the sulphides with sodium sulphide solution. The solution of the sulpho-salts of these three metals thus obtained is then treated further by the method described under 'Britannia Metal' on p. 231.

Black Copper, Raw Copper.—Black copper is not a pure smelting product, but is an alloy of copper with small amounts of iron, nickel, cobalt, zinc, antimony, arsenic, silver, gold, and bismuth. The total of these impurities in raw copper amounts to .40 to .70 per cent.

In order to determine the impurities it is most convenient to dissolve separately two 25-grm. pieces of the bright and clean sample in a mixture of 200 c.cms. water, and 175 to 180 c.cms. nitric acid of 1.20 sp. gr. To the clear solution thus obtained 25 c.cms. conc. sulphuric acid are added, the whole is evaporated to dryness, and the free sulphuric acid is expelled.

The residue is taken up with 20 c.cms. nitric acid and 350 c.cms. water, and the silver, the amount of which has been previously determined, is precipitated as chloride in this solution by the addition of the exact volume required of a standardised hydrochloric acid solution. The precipitate produced, which may contain, in addition to silver, lead and antimony, is allowed to settle, and is then filtered off. The copper is separated from the nitric acid solution by electrolytic deposition upon a platinum cone of large size, which must be frequently changed. The deposition is stopped when the solution has become colourless, in order to prevent the separation of arsenic and antimony at the kathode that would otherwise occur. The solution of the second 25-grm. portion of the copper sample is treated in a similar

manner, and the two solutions that remain after the deposition of the copper are then mixed, evaporated to dryness, taken up with hydrochloric acid, filtered, and sulphuretted hydrogen gas passed through the hot solution until a complete precipitation of the arsenic has been effected. The filtrate from this precipitate may contain iron, cobalt, nickel, and zinc, and these metals are separated in the manner described under 'Refined Soft Lead.'

The precipitate may contain, in addition to arsenic, antimony lead silver copper and bismuth, all as sulphides. Both this precipitate and that first obtained with hydrochloric acid are digested with sodium sulphide.

The solutions of the sulpho-salts thus obtained are mixed, and are then treated further as described under 'Britannia Metal' on p. 231. The residue of metallic sulphides, insoluble in sodium sulphide, is dissolved in nitric acid, the silver is precipitated by means of hydrochloric acid, the bismuth by ammonium carbonate, and the lead and copper are separated by the method described under 'Copper-Lead' on p. 178. The bismuth will be found to have partly separated with the copper first deposited, and it is therefore necessary to dissolve this copper in nitric acid, to boil this solution with excess of conc. hydrochloric acid until all the nitric acid has been displaced, to remove the excess of hydrochloric acid by further boiling, and to precipitate the bismuth and portion of the copper present as basic chlorides by the addition of a large volume of boiling water.

After allowing the precipitates of oxychlorides to settle completely, they are filtered off, dissolved in nitric acid, and the two metals separated by means of ammonium carbonate.

Electrolytic copper is analysed in the same manner, but in this case, since the impurities are less in amount, a greater weight of copper must be employed in the analysis.

Refined Copper.—This grade of copper contains cuprous oxide in addition to the impurities found in black copper. The determination of this is effected in a separate

sample as follows. A few grams of the finely divided sample is shaken with from 100 to 150 times the weight of water, containing rather more silver nitrate than is theoretically required for the amount of cuprous oxide assumed to be present.

The reaction between the oxide and the silver nitrate results in the formation of silver, basic copper nitrate, and neutral copper nitrate, the first two of which separate in the solution as a precipitate. This is filtered off, dissolved in nitric acid, and the silver separated from the copper by the method described under 'Copper-Silver' on p. 181. The calculation of the results is based on the relationship expressed by $2\text{Ag}=\text{Cu}_2\text{O}$.

Commercial Tin, Tin-foil.—Commercial tin always contains antimony, arsenic, lead, iron, and copper as impurities. In order to estimate these, a weighed portion of the sample is dissolved in aqua regia, the solution is evaporated to dryness, and, after taking up the residue with hydrochloric acid and water, sulphuretted hydrogen gas is passed through the resulting solution. The precipitate is treated with sodium sulphide solution, and the three metals, arsenic, antimony, and tin, which pass into solution, are separated as described under 'Britannia Metal' on p. 231. In this case it is necessary to dissolve the first deposit of antimony, and to redeposit the metal from the solution thus obtained, since, if the electrolysis continues for any length of time, the first deposit of antimony will be found to contain tin. The sulphides of lead and copper in the insoluble residue from the sodium sulphide digestion are dissolved in nitric acid, and these two metals separated in the usual manner (see p. 178). The iron is determined in the filtrate from the sulphuretted hydrogen precipitate.

Cast-iron, Steel, Iron Ores.—Electrolytic methods are only in use for the determination of two constituents of raw iron or iron ores—lead and copper. In order to effect the determination of these 5 to 10 grms. of the sample are dissolved in hydrochloric acid, the solution is evaporated to

dryness, taken up with hydrochloric acid and water, filtered hot, and sulphuretted hydrogen gas passed through. The precipitate of lead and copper sulphide thus obtained is dissolved in nitric acid, and the two metals are electrolytically separated by the method described fully on p. 178.

Cube-Nickel.—This commercial product contains, in addition to its chief impurity copper, arsenic, antimony, iron, cobalt, carbon, and sulphur.

The sample of metal is dissolved in aqua regia, the solution is evaporated to dryness, taken up with hydrochloric acid, the diluted solution filtered, and sulphuretted hydrogen gas is conducted through the clear filtrate. The treatment of the precipitate of sulphides thus obtained is carried out as described under some of the preceding alloys.

The filtrate is evaporated to a small bulk, and is oxidised with bromine water. After treatment with dilute sulphuric acid, if the iron present is only small in amount, an addition of ammonium hydrate is made in order to precipitate it. If the amount of iron is considerable, the solution is neutralised with sodium hydrate, acetic acid is added, and the iron is precipitated as basic acetate.

The iron may be determined in these precipitates either gravimetrically or by the electrolytic method described on p. 102. The nickel and cobalt contained in the filtrate from the precipitate of iron are determined together, according to the method given in detail on p. 106. The separation of the two latter metals must then be carried out by the gravimetric methods of analysis.

Nickel-Speiss, Raw Nickel.—Nickel-speiss consists mainly of a compound of nickel, iron, copper, and cobalt, with arsenic and sulphur.

In order to analyse this mineral, 1 grm. of the finely ground sample is dissolved in aqua regia or in forming nitric acid, and the solution thus obtained is evaporated to dryness. The residue is taken up with hydrochloric acid and water, the solution is heated, and sulphuretted hydrogen gas is then conducted through it until cold. The precipi-

tate of copper and arsenic quickly settles ; it is filtered off and dissolved in a small quantity of nitric acid. This solution may be converted by chemical means into an ammoniacal one, and the copper then separated from the arsenic by the method described under 'Copper-Arsenic' on p. 186. It is, however, better to treat the nitric acid solution with sodium hydrate and sodium sulphide. The antimony and arsenic which pass into solution are separated according to the method given on p. 201. The copper remains undissolved as copper sulphide, and is electrolytically deposited from its nitric acid solution as described under 'Copper' on p. 93. The filtrate from the precipitate obtained with sulphuretted hydrogen is evaporated to dryness after addition of a small quantity of potassium chlorate. If the amount of iron present is under 4 per cent., the residue is taken up with sulphuric acid, and ammonium hydrate added in excess. The precipitate of iron as hydroxide is filtered off, and the metal determined either by the gravimetric or electrolytic method. The filtrate from the ferric hydrate is electrolysed in order to separate the nickel, as described under 'Nickel' on p. 106.

If the amount of iron present exceeds 4 per cent., the residue that remains after evaporation is dissolved in a small amount of hydrochloric acid, the solution is made slightly alkaline with sodium hydrate, and the iron is precipitated as basic acetate by the addition of acetic acid and by boiling. The further treatment for the determination of the nickel and the iron is then carried out as described above.

Raw nickel from the lead-smelting works contains the same constituents as nickel-speiss, and it may therefore be analysed by the method described for the latter. Since, however, there is as a rule no necessity to determine any constituents beyond the copper and nickel, a shorter method may be employed.

The solution is prepared by dissolving 1 grm. of the finely powdered sample in hydrochloric acid containing

bromine, and is evaporated to dryness in order to drive off the arsenic. This evaporation is repeated many times with fresh amounts of the acid. The residue is then taken up with a few cubic centimetres dilute sulphuric acid, and the solution is again evaporated until white fumes appear. Water is then added, sulphuretted hydrogen gas is conducted through the solution, and the precipitate of sulphides is filtered off.

This precipitate is then ignited in order to drive off any remaining traces of arsenic or antimony, and, after cooling, the copper oxide is dissolved in nitric acid, and the metal deposited electrolytically.

The filtrate from the sulphides precipitate is oxidised with bromine water, the iron is precipitated with ammonium hydrate and filtered off (this requires repeating, after re-solution of the first precipitate), and the filtrate is evaporated to dryness. The residue is ignited with ammonium chloride, in order to remove the zinc as zinc ammonium chloride.

The remaining salt is brought into solution with dilute sulphuric acid and water, and, after addition of an excess of ammonium hydrate, the nickel is electrolytically deposited under the conditions given on p. 106.

Nickeliferous Magnetic Pyrites; Arsenical Cobalt and Nickel Ores; Roasted Cobalt Slimes from Colour Works; and other Nickel and Cobalt Smelting Products.—These products and substances are treated by methods exactly similar to those described for nickel-speiss and raw nickel.

Copper Regulus and Lead Matte.—Copper regulus and lead matte contain, in addition to copper and lead, much iron, sulphur, and silica. It is sufficient for most practical purposes to know the percentage of copper and lead. In order to effect the determination of these two constituents, 1 gm. of the finely powdered substance is dissolved in 30 c.cms. nitric acid, and the solution after boiling is diluted with hot water and filtered. The lead is then separated from this solution as peroxide at the anode by electrolysis. When the lead deposition is completed, the kathode bearing

the greater portion of the copper is dipped into the remaining acid electrolyte, and the whole of the copper is allowed to pass again into solution. The solution is evaporated to dryness with sulphuric acid, the residue is taken up with water, and the copper is precipitated by boiling with sodium hyposulphite or by conducting sulphuretted hydrogen through the solution. The precipitate of sulphides is filtered off, ignited, and the oxide dissolved in nitric acid; from this solution the copper is electrolytically deposited. It is not possible to effect a direct separation of the copper, since the traces of arsenic, antimony, and silver present in these products would be deposited at the kathode with the copper, and the large amount of iron present would exercise a disturbing influence.

Cupriferous Pyrites; Burnt Pyrites.—In cupriferous pyrites, and in lixiviated or unlixivated roasted products, it is chiefly necessary to know the percentage of copper.

About 5 grms. of the finely powdered sample is treated with hydrochloric acid, to which later some nitric acid is added, and the solution of the soluble portion of the ore is effected with the aid of gentle heat. The liquid is then evaporated nearly to dryness to remove the excess of nitric acid, the diluted hydrochloric acid solution is filtered, and sulphuretted hydrogen is passed through the filtrate. The precipitate will contain lead, copper, and arsenic as sulphides, and is treated for their separation as described under the last product.

Copper Ashes, Copper Matte, Copper Slags, Flue Dust.—The copper in cupriferous ashes and some other furnace by-products may be extracted by simple digestion with nitric acid. The copper is then separated from this acid solution by electrolytic deposition.

Those products which do not dissolve in nitric acid require treating by the method described under 'Copper Regulus.'

Galena.—This natural ore of lead contains principally lead sulphide, but small amounts of copper, iron, silver, antimony, arsenic, and zinc are always present with the lead.

If the amount of antimony is not great, the finely ground sample of the ore is treated with conc. nitric acid, and after the oxidation is completed the solution is diluted, filtered from the gangue, and the filtrate evaporated to dryness.

The residue is taken up with hydrochloric acid and hot water, and sulphuretted hydrogen gas is then passed through the hot solution. The liquid is allowed some time to settle, and is then filtered. The precipitate is treated with ammonium carbonate solution in order to extract the arsenic, with sodium sulphide solution to remove the antimony, and the residue (part of it only, if more than 1 gm. ore has been used) is then dissolved in nitric acid, and the copper separated from the lead by the electrolytic method.

If the galena be one containing exceptionally large amounts of antimony, a separate portion of the sample weighing a few grams is treated with nitric and tartaric acids, and the liquid is then made up to a definite volume. A measured portion of this is withdrawn, the lead is precipitated as lead sulphate by means of sulphuric acid, and the filtrate is treated with excess of sodium hydrate and with sodium sulphide.

The solution of the sulpho-salt of antimony thus obtained is then used for the electrolytic deposition of that metal as described under 'Antimony' (see p. 146). The filtrate from the first precipitate with sulphuretted hydrogen contains zinc and iron. It is oxidised by means of bromine water, the iron is precipitated by ammonium hydrate, and the zinc is determined either volumetrically or by one of the electrolytic methods given under 'Zinc' on p. 114.

The silver is most accurately determined in galena by

the dry method. Very frequently it will be found that the analysis is most successfully performed by determining the individual metals in different test-samples of the ore. In all cases the lead and the gangue are first removed, by dissolving the ore in nitric acid, evaporating with sulphuric acid to dryness, and filtering off the insoluble portion and the lead sulphate.

Roasted galena is treated in exactly the same manner as galena, with the exception of the preparation of the solution of the ore. This is effected by direct treatment with aqua regia, repeated evaporation to dryness with hydrochloric acid, and final solution of the residue in hydrochloric acid and water.

Fahl Ores ; Tetrahedrite.—The different fahl ores contain arsenic, antimony, lead, zinc, iron, and silver. If no arsenic be present in the ore, 1 grm. of the finely ground sample is dissolved in 15 c.cms. aqua regia, the solution is evaporated to dryness, the residue brought into solution by means of hydrochloric acid and water, and the separation of the individual metals then effected by the methods described under 'Galena.' The silver will be found in the residue from the first solution of the ore ; its amount is most satisfactorily determined by operating by the dry method upon a larger amount of the ore.

If arsenic be present, the ore is opened up by means of 10 c.cms. nitric acid in place of aqua regia.

Tin-stone.—This ore of tin consists principally of tin and iron oxides. In order to open up the ore, the very finely ground sample is fused with 3 parts sodium hydrate and 3 parts sulphur. The melt when cold is lixiviated with water, an excess of sodium sulphide solution is added, and the further conduct of the analysis follows that described under 'Commercial Tin' on p. 238.

The residue from the melt and lixiviation contains the iron and the other impurities of the ore. These are separated by the methods already described.

Stibnite.—This ore of antimony is a sulphide of the

metal, containing iron, lead, copper, and arsenic as impurities. The opening up of the finely ground sample of ore for analysis is achieved by fusing with sodium hydrate and sulphur as in the case of tin-stone.

The melt is lixivated with water, an excess of sodium sulphide is added to the solution, and the antimony is electrolytically determined in the filtered liquid by the method given under 'Antimony' on p. 146. The arsenic is determined in the remaining electrolyte.

The residue that remains after lixiviation of the melt contains the lead, copper, and iron. It is dissolved in nitric acid, and the two former metals are electrolytically separated in this solution by the method described fully under 'Copper-Lead' on p. 178. The iron remains in solution, and, after conversion of the nitrate into sulphate, it is determined by electrolytic deposition.

The above series of practical examples does not contain references to all the cases in which electrolytic methods are now being employed, or in which they might be employed, for the analysis of alloys, furnace by-products, metals, or ores. These examples are given chiefly as a guide to the various ways in which electrolysis may be used as an aid to the ordinary methods of analysis. It will always be found most convenient to combine the chemical and electrolytic methods of separation; and, rightly used, the latter will take an independent place by the side of the gravimetric and volumetric methods which have hitherto been solely employed in analytical work.

APPENDIX

Theoretical Percentage of the Metallic Elements in certain Metallic Salts.

No.	Name of Salt	Chemical Formula	Percentage
1	{ Antimonyl Tartrate (Tartar-emetic) . }	$C_4H_4(SbO)KO_6 + \frac{1}{2}H_2O$	36.14 Sb
2	Bismuth Nitrate .	$Bi(NO_3)_3 + 5H_2O$	42.91 Bi
3	Cadmium Sulphate	$CdSO_4 + 4H_2O$	40.00 Cd
4	Cobalt Sulphate .	$CoSO_4 + 7H_2O$	20.92 Co
5	Cobalt Chloride .	$CoCl_2 + 6H_2O$	24.71 Co
6	Copper Sulphate .	$CuSO_4 + 5H_2O$	25.33 Cu
7	Copper Chloride .	$CuCl_2 + 2H_2O$	37.06 Cu
8	Ferrous Sulphate .	$FeSO_4 + 7H_2O$	20.14 Fe
9	{ Ferrous Ammo- nium Sulphate }	$FeSO_4(NH_4)_2SO_4 + 6H_2O$	14.28 Fe
10	Gold Chloride .	$AuCl_3 + 2H_2O$	57.98 Au
11	Lead Nitrate .	$Pb(NO_3)_2$	{ 62.54 Pb 72.21 PbO ₂
12	{ Manganese Sul- phate . }	$MnSO_4 + 7H_2O$	{ 19.85 Mn 31.40 MnO ₂
13	Manganese Nitrate	$Mn(NO_3)_2 + 6H_2O$	{ 19.16 Mn 30.31 MnO ₂
14	Mercuric Chloride .	$HgCl_2$	73.80 Hg
15	Nickel Sulphate .	$NiSO_4 + 7H_2O$	20.94 Ni
16	Nickel Chloride .	$NiCl_2 + 6H_2O$	24.72 Ni
17	Platinic Chloride .	$PtCl_4 + 5H_2O$	45.56 Pt
18	{ Potassium Chloro- platinate . }	K_2PtCl_6	40.00 Pt
19	{ Potassium Auric Chloride . }	$AuCl_3.KCl + 3H_2O$	42.05 Au
20	{ Potassium Ferric Sulphate (Iron Alum) }	$Fe(SO_4)_3.K_2SO_4 + 24H_2O$	11.12 Fe
21	{ Potassium Ferric Oxalate . }	$Fe_2(C_2O_4)_3.3K_2C_2O_4 + 6H_2O$	11.40 Fe
22	Silver Nitrate .	$AgNO_3$	63.52 Ag
23	Stannous Chloride	$SnCl_2 + 2H_2O$	52.04 Sn
24	Zinc Sulphate .	$ZnSO_4 + 7H_2O$	22.68 Zn

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